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FOAM STABILIZATION USING WOOD POLYMERS

Master´s Programme in Chemical, Biochemical and Materials Engineering
Major in Fibers and Polymers Engineering

Master's thesis for the degree of Master of Science in Technology
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Abstract

Research and Industry alike are coming to a level of awareness that dictates the use of greener material, seeking materials that have lower environmental impact, are recyclable, and at the same time functional and affordable. Many companies are compelled to find replacements for some of the major polluters with viable and affordable alternatives. Thus, natural foams can be used to replace synthetic polymers used for thermal insulation or packaging. There are many challenges in replacing conventional synthetic materials with natural counterparts, some of which include having regular access to the raw materials and producing them with little modification in order to minimise the environmental impact.

The main aim of this thesis was to prepare stable natural foams using wood polymers. The foams are intended to function outdoors and be disposable in nature without having any environmental side effects. That is why the foams needed to be completely natural with the least amount of modifications possible.

The foams were prepared by mixing wood polymers, surfactant, and water, using a homogenizer for efficient integration and aeration. The wood polymers used were lignin and cellulose in different fibrillation states, that is, cellulose nanofibrils (CNF) and macrofibres (bleached and unbleached pulp). The bleached pulp proved to provide the best stability for the longest period of time, compared to the other materials tested. The lignin provided little support, but supplied the foams with a natural dark brown colour. Alternatively, the foams could be dyed light green by using chlorophyll. Sodium dodecyl sulfate (SDS) and Tween 80 were the two main surfactants used. SDS produced more foam that remained stable for longer time than Tween 80.

The natural foams studied in this thesis are promising materials for outdoor thermal insulation applications. Thermal insulation and resistance to weathering conditions should be investigated further in future research regarding this topic.

Keywords Natural foams, wood, polymers, lignin, cellulose, thermal insulation

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I would like to express my sincerest thanks to my supervisor professor Monika Österberg for offering me this great opportunity to work on this master's thesis topic, and for her support and guidance along the way. I would also like to thank my advisor Juan Jose Valle Delgado for his relentless support and patience.

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Karim Bassily

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List of abbreviations

CLP	Colloidal lignin particles
CNC	Cellulose nanocrystals
CNF	Cellulose nanofibres
CTAB	Cetyltrimethylammonium bromide
GTMAC	Glycidyltrimethylammonium chloride
SDBS	Sodium dodecyl benzene sulfonate
SDS	Sodium dodecyl sulfate
THF	Tetrahydrofuran

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1 Introduction:

Foams have been extensively used in recent years, whether for building insulation, packaging, or as fire retardants, mainly due to their unique characteristics and wide variety. As a result, petroleum based foams have garnered a large market prominence. With the rise of environmental awareness, striving to reach environmentally friendly foams is gaining attention from research and industry alike. Natural foams could replace artificial foams in few general applications like in building insulation or packaging, or in some niche applications such as in oil recovery or firefighting (Langevin, 2017).

The main objective of this thesis is to find stable natural foams under consistent lab conditions. Different natural materials from wood and surfactants have been tested in order to produce the most stable foams. Depending on the application, lab conditions could be different from real-life conditions. Nevertheless, lab experiments can help to discriminate what materials and combinations perform better as foam stabilizers, which then could be tested in real-life conditions in the next stage.

The natural foams of this thesis are intended for different outdoor applications, including thermal insulation. The foams should be weathering resistant, nontoxic and have natural colours.

2 Literature review

2.1 Natural wood polymers:

2.1.1 Cellulose:

As the main building block in all plants and trees, it is the most abundant natural polymer on Earth. Cellulose has a linear polymer chain composed of glucose molecules. As the most ubiquitous material in plants, it forms the major structure of the cell walls, combined with lignin, hemicellulose, and pectin.

Cellulose is composed of D-glucose units that have 4C1-chair configuration. Those units are bonded with β-1,4-glycosidic bonds, which result in the units turning 180° alternatively (Rojas, 2016). Figure 1 shows the structure of a representation of cellulose molecule. Cellobiose, half of the molecule shown in Figure 1, can be considered the repeating unit in cellulose (Rojas, 2016; Krässig, 1993).

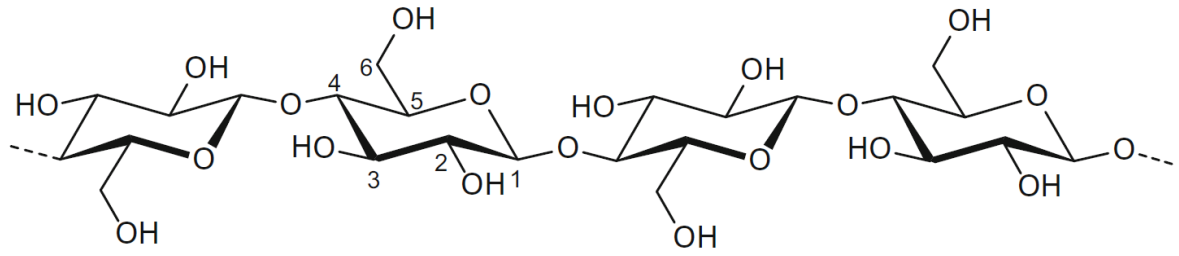

Figure 1: Cellulose molecule representation, Figure adapted from Rojas, O.J. (2016).

Cellulose has a hierarchical structure in plants, starting from sizes visible to the naked eye, to nano sizes. The hierarchical structure of cellulose is shown in Figure 2. Cellulose usually has chains ranging from 500-15,000 nm (Rojas, 2016), those chains are packed into fibrils, typically reaching up to few micrometres in length and with a diameter of 1.5 to 3.5 nm. The fibrils are assembled together to form bundles, called microfibrils, ranging from 10-30 nm in diameter. Macrofibrils consist of many microfibrils and vary in size depending on their source, and many macrofibrils create a fibre in a plant (Rojas, 2016; Klemm et al., 2005).

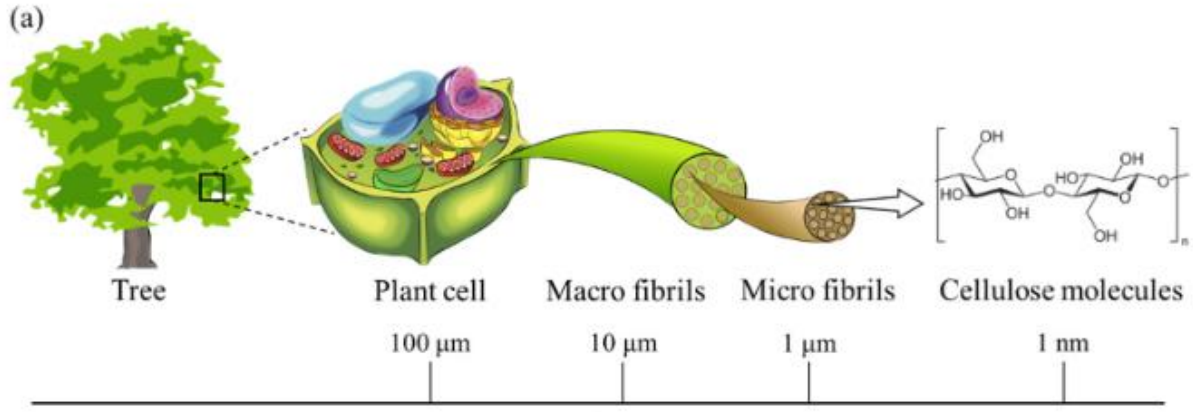

Figure 2: Hierarchical structure of cellulose in trees. Figure adapted from Miyashiro et al. (2020).

Paper is one of the earliest products ever made using cellulose and nowadays it is one of its main industrial products. For papermaking, cellulose fibres are mainly produced from wood chips through the kraft process, where lignin and extractives are removed to liberate cellulose fibres. Cellulose can also be used for packaging, like in a research paper by Assis et al., cellulose acetate was mixed with norbixin, zeaxanthin or lycopene to create a packaging film for food grade products (Assis et al., 2020). Cellulose has also been used in textiles for many years, but recently, it has been combined with regenerated cellulose for improved properties such as better UV protection, as demonstrated by Kocić et al (2019). In construction, there are applications utilizing cellulose materials that can replace fossil-based ones in order to reduce the greenhouse gas emissions from their production processes. Revuelta-Aramburu et al. compares the production processes of conventional construction material for insulation, like polyurethane foam, against cellulose based material like plant fibre blocks (PFB). In their comparison, Life Cycle Assessment for each material was analysed and has shown how much PFBs are less impactful compared to their synthetic counterparts (Revuelta-Aramburu et al., 2020). Cellulose is also used in consumables and drugs, where it can be used as an inactive filler. While in many foods, microcrystalline cellulose is used as an emulsifier, known as E460i.

Those are some of many common applications that cellulose plays a major role in. There are many niche applications being researched like using flexible cellulose paper for electronics, to replace synthetic insulators (Koga et al., 2020), and using wood cellulose paper as substrate for solar panels, which should cheapen the production process while making it more environmentally friendly (Fang et al., 2020).

2.1.2 Hemicellulose

As one of the main constituents of plants, hemicellulose plays a major role in plant structures. After cellulose and lignin, hemicellulose is the third most important constituent in plants and trees.

There are different kinds of sugars that result in different forms of hemicellulose, including xylan, glucuronoxylan, arabinoxylan, glucomannan, and xyloglucan. On the other hand, cellulose only consists of anhydrous glucose.

Hemicellulose is composed of shorter polymers compared to cellulose. While hemicellulose has around 500 to 3,000 units, cellulose has from 7,000 to 15,000 units. Also, hemicellulose is branched, unlike cellulose (Gibson, 2012).

2.1.3 Lignin

One of the main structural components in all trees, it is the second most common natural polymer, after cellulose. Lignin is a main by-product of the paper industry, as its colour is undesired. The most common usage of lignin nowadays is to burn it as a fuel. While it has plenty of useful properties, like its hydrophobicity, antioxidant and antimicrobial properties (Ponomarenko et al., 2015; Alzagameem et al., 2019), that can be utilised for many applications, it is of limited production. As a result, the potential of it being used over a large scale in industry in the near future is restricted.

Lignin is a amphiphilic molecule with both hydrophilic and hydrophobic moieties, it is dark brown in colour, which results in the visible rich colour of wood. It is a heterogeneous molecule that has a complicated structure varying with species and method of isolation.

As being more hydrophobic than cellulose and highly rot resistant, it is a vital component in wood, and it acts as a gluing material and thus increases the rigidity of cell walls and ultimately the wood itself (Gargulak et al, 2015).

Kraft lignin as a standalone molecule has very limited usage, but in a form of a dispersed solution, it has a higher potential for a wide array of applications. Common examples of such dispersions include colloidal lignin particles (CLPs) (Österberg et al., 2020).

CLP are dispersions prepared from kraft lignin, preparation is a simple process, however it is limited to lab scale production thus far. In a research article published by Lintinen et al., lignin was mixed with THF and ethanol in order to produce CLPs. In this article the process was an attempt to create a process that could be adopted by the industry (Lintinen et al., 2018), this has not been realised yet.

Lignin can be chemically modified to create cationic lignin, which can be used for example to turn cationic CLPs anionic. Due to its solubility in water cationic lignin could also be used as an emulsifier like lignosulfonates. Cationic CLPs can stabilize a wider array of pickering emulsions compared to kraft lignin or CLPs (Sipponen et al., 2017).

2.1.4 Lignocellulosic nanoparticles

Lignocellulosic particles are nanoparticles that contain lignin or cellulose. They are going under extensive research to replace synthetic counterparts to become utilized in many applications. Two common examples of lignocellulosic nanoparticles are cellulose nanocrystals (CNC) and cellulose nanofibers (CNF), both derived from cellulose. The CLPs made of lignin commented in the previous section are another example of lignocellulosic nanoparticles. Both materials are environmentally friendly and safe to use, and that resulted in a lot of research centred around them.

CNCs, obtained by acid hydrolysis of pulp, have many interesting properties that allowed them to be used in many different applications, including but not limited to applications in fields like biomedical engineering, in drug delivery, and material sciences (George et al., 2015).

CNFs are usually produced through mechanical fibrillation from pulp, this process can be assisted with chemical or enzymatic pretreatment (Kang et al., 2006). Liu et al. demonstrated the effects of using enzyme pretreatment on mechanical fibrillation of CNFs. With generally positive results, the CNFs lost some mechanical strength but produced higher yield, more uniformity in diameter of the fibrils, and saved 60% of energy consumption. It was stated that this process is still viable commercially and is environmentally more friendly with the energy saved (Liu at al., 2019).

2.2 Foams

2.2.1 General description

A foam is a formation of gas trapped into a liquid or solid structure. With many variations, foams can be mainly divided into two types: liquid and solid foams (Figures 3 and 4). Foams have many different applications that range from day to day to industrial applications. They are essential in cooking processes, detergents, fire extinguishers, insulation and many other applications.

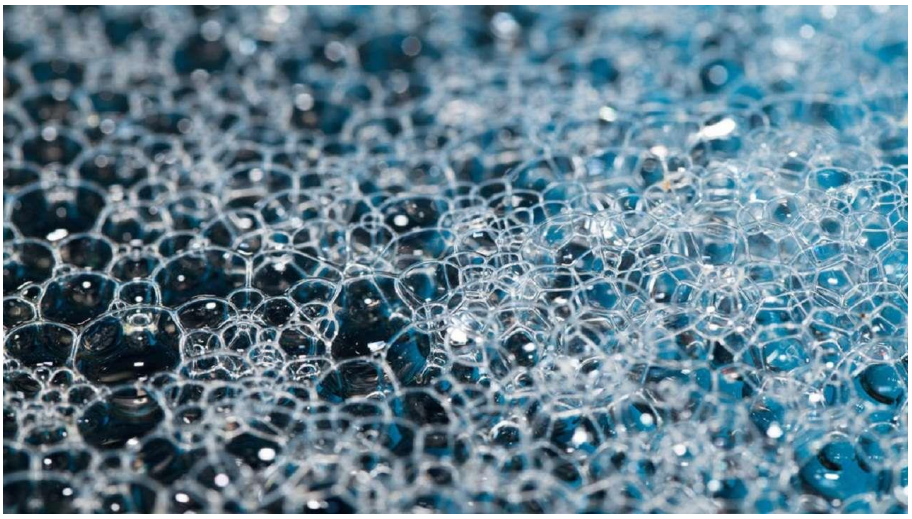

Figure 3: Soap bubbles, a type of liquid based foam. Figure adapted from PTI (2018).

Liquid foams are formed when gas bubbles are trapped within a liquid. Usually the liquid forms very thin films trapping the air, creating bubbles. In contrast, solid foams usually appear like a solid material containing air bubbles trapped within. For both types, the air could have been produced by a chemical reaction within the liquid or solid structure, producing the gas (e.g. Yeast producing CO_2 in bread dough) or it could have been injected manually by an external air supply.

Figure 4: Variety of polyurethane foams, a type of solid foam. Figure adapted from The Polyurethanes team (2015).

The importance of foams is attributed to their versatility, they can be altered to conform to certain specifications if desired, allowing them to be utilised for a variety of applications while employing them with highest efficiency.

Some of the prominent applications for foams nowadays include the use in fire extinguishers. Fire extinguisher foams were originally created as a solution to oil fires, as water was too dangerous and ineffective to use in such situations. Another common application is in detergents, like in soap, which lathers producing foam when mixed with water. In baking, yeast in dough converts sugars to carbon dioxide, creating bubbles and resulting in a leavened bread. On a larger scale, solid foams are commonly used in construction and insulation. Polystyrene is commonly used in packaging and insulation, it can contain up to 95% air (Polystyrene, 2020) and proved to be invaluable for many industries. Another common solid foam used is polyurethane, it is used in many different fields as its properties can be altered drastically. It has some uses in construction, furniture, transportation, and many others, as a result it is treasured in those industries.

2.2.2 Foam stabilization:

In order to maximise the functionality of foam, it is essential to keep it stable for the longest time possible. Having a more stable foam, means more functionality and higher value. Water, air, and a surfactant are essential components to create a liquid foam.

There are many factors that affect the stability of foams. Drainage reduces the thickness of the liquid films between bubbles, decreasing the stability of the foams. Ostwal ripening, that is, the diffusion of air from the smaller bubbles to the bigger ones, also destabilizes the foams. On the contrary, electrostatic, steric, and hydration repulsions between surfactant layers adsorb at the air-water interface of the bubbles can stabilize the foams (Kronberg et al., 2014). The Maragoni effect, which occurs when there is a gradient in surface tension at an interface between two phases or different materials, can also make the foams more stable (Anazadehsayed et al., 2018).

Surfactants are amphiphilic compounds that contain a hydrophilic head and a hydrophobic tail, due to their nature they move towards interfaces, between water and oil for instance, or between water and air when in foams. Surfactants play a major role in stabilizing foams, by reducing surface tension, or through repulsive interactions like inducing steric hindrance. They are commonly used in detergents, soaps, adhesives, and many emulsions (Paria, 2008).

For the stability of foams, solid particles are often introduced, for water and surfactants alone do not form very stable foams for long time, which prevents the foams from being utilized in many applications. Kruglyakov et al. made an extensive study around properties of foam and foam films stability by solid particles, concluding to very positive results. The particles used include Aerosil (added to increase the contact angle in the foams), potassium chloride (for increased conductivity), and aluminium hydroxide (Kruglyakov, 2011). Azdarpour et al. studied foam stabilization by adding synthetic polymers. They proposed that polymers can be used to increase viscosity in the foam, thus decreasing its drainage rate. Polyacrylamide polymer, sodium dodecyl sulfate (SDS) and sodium dodecyl benzene sulfonate (SDBS) surfactants were used. Their results show that higher molecular weight polymers provided better foam stability, and that foam stability and polymer concentration in the foam were directly proportional (Azdarpour et al., 2013).

2.2.3 Natural polymers in foams:

Other than cellulose and wood polymers mentioned earlier, there are other polymers that are commonly used in foams, like alginate. These polymers have common usage in research attempting to replace synthetic polymers. While synthetic polymers are usually easy to control and characterise, natural polymers are more challenging. Those challenges arise due to their polydispersity, usually resulting from the polymers different sources, chemical structure and functional groups. In order to maintain producing natural polymers sustainably, they should be produced with as few modifications as possible. Utilising natural polymers to their fullest extent is a challenge that is amplified by the need to remain sustainable, this demonstrates the importance of research in this field.

In a research published by Al-Qararah et al., foam with cellulose fibres was prepared by using Kraft fibres (obtained from wood pulp) and SDS. However, the fibres did not adsorb to the interface (Al-Qararah et al., 2013). CNF foam was created by Cervin et al., octylamine was added to reduce the charge density of the CNF. The result was that the CNF was attracted to the air-liquid interface thanks to the octylamine (Cervin et al., 2013).

Lignin is considered another viable material to use in creating natural foams. Lignin molecules can adsorb at air-liquid interfaces, increasing stability in natural foams. Yang et al. used alkaline lignin nanoparticles for stabilisation in emulsions, which in turn were used to prepare solid foams, which were utilized to adsorb metallic ions from a solution (Lam et al, 2014; Yang et al., 2013).

In an article by Mimini et al., lignin was used in preparing polyurethane foams. Polyurethane foams contain polyols and isocyanates, and by preparing lignin polyols from kraft lignin, it can replace the fossil-based polyols used in polyurethane. That decreases the toxicity of polyurethane, resulting in a greener production process (Mimini et al., 2018; Obaid et al., 2016).

Lignin aerogels have been prepared by Perez-Cantu et al. for thermal insulation. The lignin was extracted from Liquid Hot Water of wheat straw pretreatment. Lignin was crosslinked with oligo(ethylene glycol) and oligo(propylene glycol)-α,ω-diglycidyl ethers to produce a hydrogel that would be converted into aerogels with positive results (Perez-Cantu et al., 2014).

Andersen et al. prepared alginate foams that contained calcium carbonate and strontium carbonate particles. The foam was prepared using a homogeniser, that was used to increase the aeration. The alginate foam was used to absorb physiological solutions, and with the possibility of being used for other medical applications as well (Andersen et al., 2014).

Furthermore, natural foams can be used for building insulation, as Wicklein et al. demonstrated in their research. By using nanocellulose, graphene oxide, and sepiolite nanorods, they produced a foam that has higher thermal resistance compared to conventional synthetic foams (Wicklein et al., 2015).

Those are few common materials that can be used in natural foams and have been under extensive research. There is high potential in utilising these materials further and reducing dependency on synthetic polymers.

2.2.4 Foam for thermal insulation:

One of the most widely utilised applications of foams is in thermal insulation (Figure 5). Usually, synthetic polymers are best optimised for that task. They are affordable, efficient, adjustable, and easy to apply.

Figure 5: A worker spraying polyurethane foam on wall for insulation. The foam sticks to the wall, expands, then solidifies. Figure adapted from BASF (2020).

As being environmentally friendly is now expected and pursued, many companies and research facilities are trying to replace every non-biodegradable material with bio-degradable ones.

For thermal insulation, polyurethane is the most commonly used material for foam, it is efficient, foams easily, and is cheap. Natural foams require natural polymers that are not readily available, do not foam as easily, are more expensive to obtain or are usually utilised for other industries.

In an article published by Wicklein et al., natural foams have been created for thermal insulation using nanocellulose, graphene oxide, and sepiolite nanorods. This foam is intended as an insulating construction building material, made to replace conventional insulating synthetic polymers, and has shown promising results. It is fire-retardant, anisotropic, and has shown to have higher thermal insulation capabilities compared to synthetic polymers used for insulation (Wicklein et al., 2015). Thermal insulation in buildings is a crucial necessity, and decreasing heat loss while utilizing greener materials is invaluable nowadays.

3 Materials and Methods

3.1 Materials:

The kraft lignin used was UPM BioPiva 100, provided by UPM and extracted from pine tree. The CLPs and cationic lignin were prepared from the same lignin. Never-dried bleached kraft pulp from birch supplied by Finnish pulp mills and unbleached birch pulp provided by Kaukas mill were used in this work. CNF was prepared at the Department of Bioproducts and Biosystems of Aalto University by mechanical fibrillation of never-dried bleached kraft birch pulp using a high-pressure fluidizer (Microfluidics, M-110Y, Microfluidics Int., Co., Newton, MA). No chemical or enzymatic pretreatments were applied before fibrillation. Chlorophyll was extracted from tomato leaves and kindly provided by Tia Lohtander (Department of Bioproducts and Biosystems, Aalto University). Two different Tween 80 (Polysorbate 80) were used, both were provided by Sigma-Aldrich, with CAS: 90 05-65-6. SDS was provided by Sigma-Aldrich, with CAS: 151-21-3. Cetyltrimethylammonium bromide (CTAB) was provided by Fluka chemicals with CAS: 3282-73-3.

3.2 Methods:

3.2.1 Preparation of Colloidal Lignin Particles:

CLPs were prepared according to the protocol published by Sipponen et al. (Sipponen et al, 2017). Briefly, the lignin is mixed with a solution of acetone and water until it dissolved. Then, the mixture was filtered using a büchner funnel. CLPs were formed when water was added to the solution. Acetone was evaporated in a rotary evaporator and the dispersion was concentrated by using the ultrafilter (Lintinen et al, 2018).

3.2.2 Preparation of cationic lignin:

Cationic lignin was prepared according to the procedure described by Sipponen et al. The reaction started by adding 500 ml of 0.2M NaOH (sodium hydroxide) to 5 g of dry weight lignin. The components were placed in a 3-necked flask, in an oil bath at 70°C, they were left to mix and reach the temperature of the oil bath. Afterwards, 17.7 ml GTMAC

(Glycidyltrimethylammonium chloride) were added drop wise. The reaction was left for 2 h. Above the reactor, there was a condensation tower and cooling water. Then, the flask was moved to an ice bath, while being mixed, HCL (hydrochloric acid) was added till the mixture was neutral. Finally, the cationic lignin was dialyzed for few days using a 1 kDa dialysis tubing (Sipponen et al., 2017). In order for the cationic lignin to be used in a comparable sample volume to other samples, the cationic lignin solution was concentrated using a rotating evaporator (Buchi Rotavapor, R210).

3.2.3 Preparation of foam and stability measurements:

In order to prepare the foams, all components were mixed using a homogeniser, IKA T18 basic Ultra-Turrax. First, 25ml of deionised water, a specific wood-polymer (e.g. lignin, CNF, etc.), and surfactant were all added into a beaker. The components were then mixed using the homogeniser for 2 minutes at a standard speed (approx. 16200 rpm), then transferred to a graduated cylinder where the foam volume was accurately measured at different times.

4 Results and discussion

In this section, a detailed analysis of the foams formed by the dispersions of different natural materials is presented. All materials were tested with different surfactants and under similar conditions. The effects of different materials, surfactant types and concentrations on foam volume and foam stability are shown in the graphs below.

Bar charts present the foam volume inside the graduated cylinders at certain times, whereas foam volume versus time graphs show the stability of the foams up to 8 h – or 24 h for some samples.

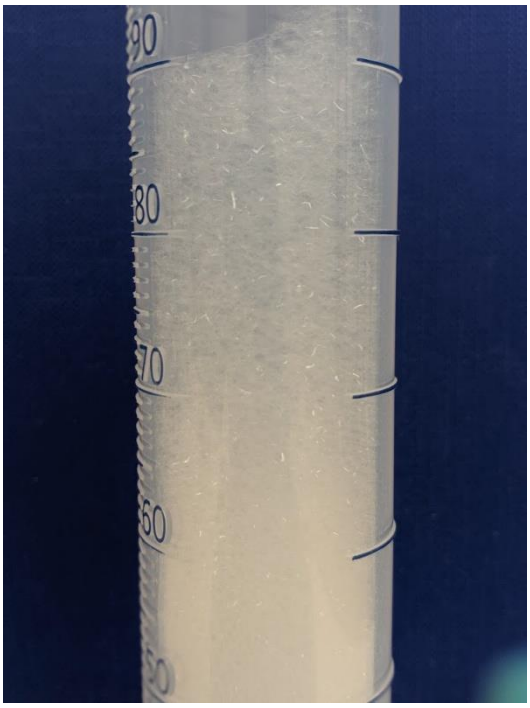

Figure 6: CNF foam containing 0.058 g dry weight CNF

4.1 Foam stabilization by CNF

CNF was the first material used as a stabilizer for the foams in this research. It was added in varying concentrations to study its effects on foam stability. The foam volume was measured for three samples with different concentrations of CNF. A CNF foam sample in a graduated cylinder is shown in Figure 6. It contained 0.058 g dry weight CNF, 0.075 g Tween 80 and 25 ml deionised water.

The effect of the amount of CNF on the foam formation and foam stability are shown in Figure 7, where all samples contained 0.75 g of Tween 80 and 25 ml deionised water. The 0.058 g CNF sample seems to have better foamability at initial times. Lower CNF concentrations did not seem to provide that good support for the foam, whereas higher CNF concentrations could be too dense for proper foam formation. Nevertheless, the differences in foam volume between the different samples decreased with time and became small after 8 h.

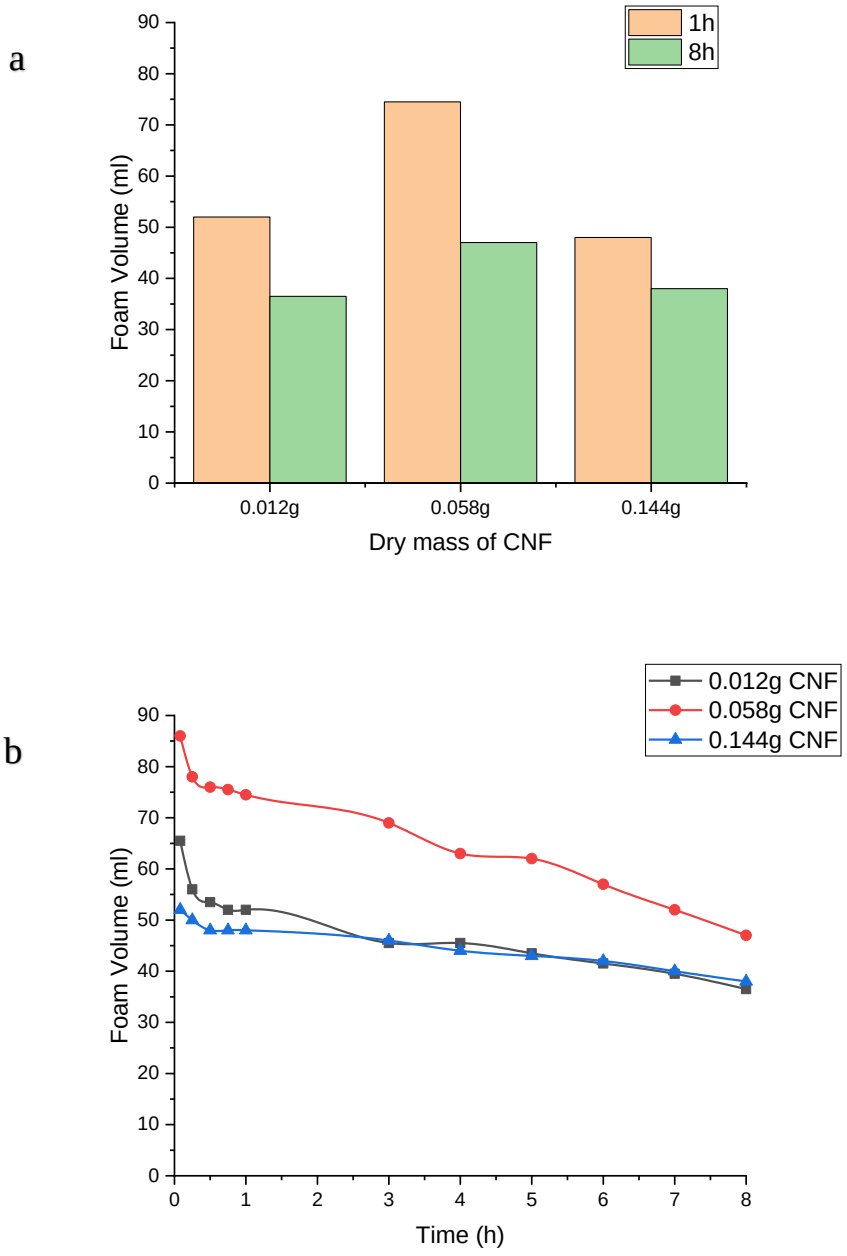

Figure 7: Foamability of CNF dispersions; a) foam volume of CNF samples with different CNF dry masses at 1 and 8 h after preparation; b) time evolution of foam volume of CNF samples. All the samples contained 0.75 g Tween 80 and 25 ml deionised water.

The effect of surfactant type and concentration on the CNF foams is presented in Figure 8. All samples contained a dry weight of 0.058g of CNF and 25ml deionised water. Figure 8a shows the foam volume compared at 1 and 6 h after preparation time and Figure 8b shows the foam volume against time over 6 h. Figure 8 shows that similar results were obtained for all the SDS samples studied, which means that we could use lower SDS concentrations without affecting the foam formation and stability. Tween 80 gives similar results than SDS when 0.75 g were

used, but the foamability decreases significantly at lower surfactant amounts, as with the 0.15 g Tween 80 sample.

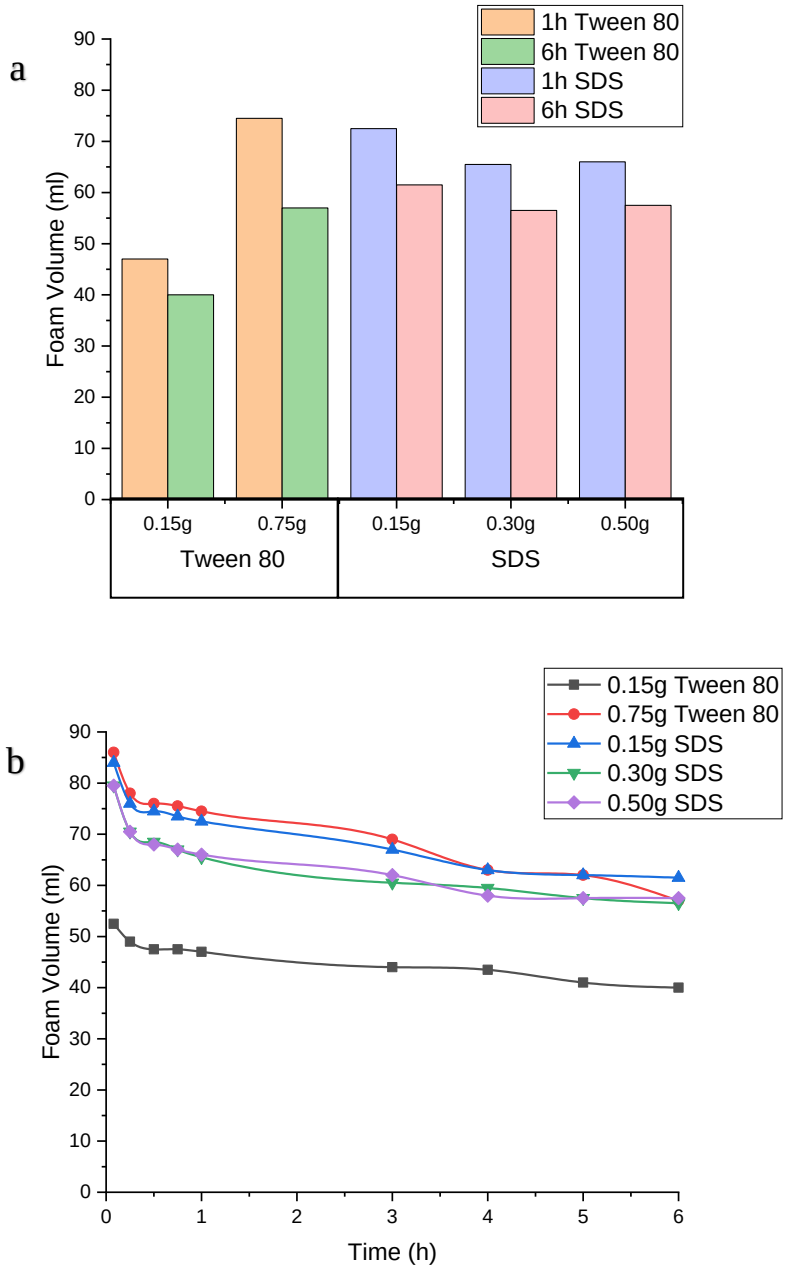

Figure 8: Foamability of CNF dispersions with different surfactants; a) foam volume of CNF samples with different concentrations of Tween 80 and SDS at 1 and 6 h after preparation. b) time evolution of foam volume of CNF samples with different concentrations of Tween 80 and SDS. All the samples contained 0.058 g CNF and 25 ml deionised water.

The effect of ions in the water on the CNF foams is shown in Figure 9. Two CNF samples were compared, with the only difference is the water used; one sample with deionised water and the other with tap water. All samples contained 0.058g dry mass CNF, 0.75g Tween 80, and 25ml

of water. Both samples show similar foam volumes in the beginning, but the tap water sample shows lower foam volume at later times in the experiment. The difference is insignificant in terms of foam volume and using tap water should not affect foam volume negatively. In addition, using tap water is more convenient for practical applications. All samples with CNF had over half of the foam left after 8h, showing that fibrils stabilizes the foam structure over time.

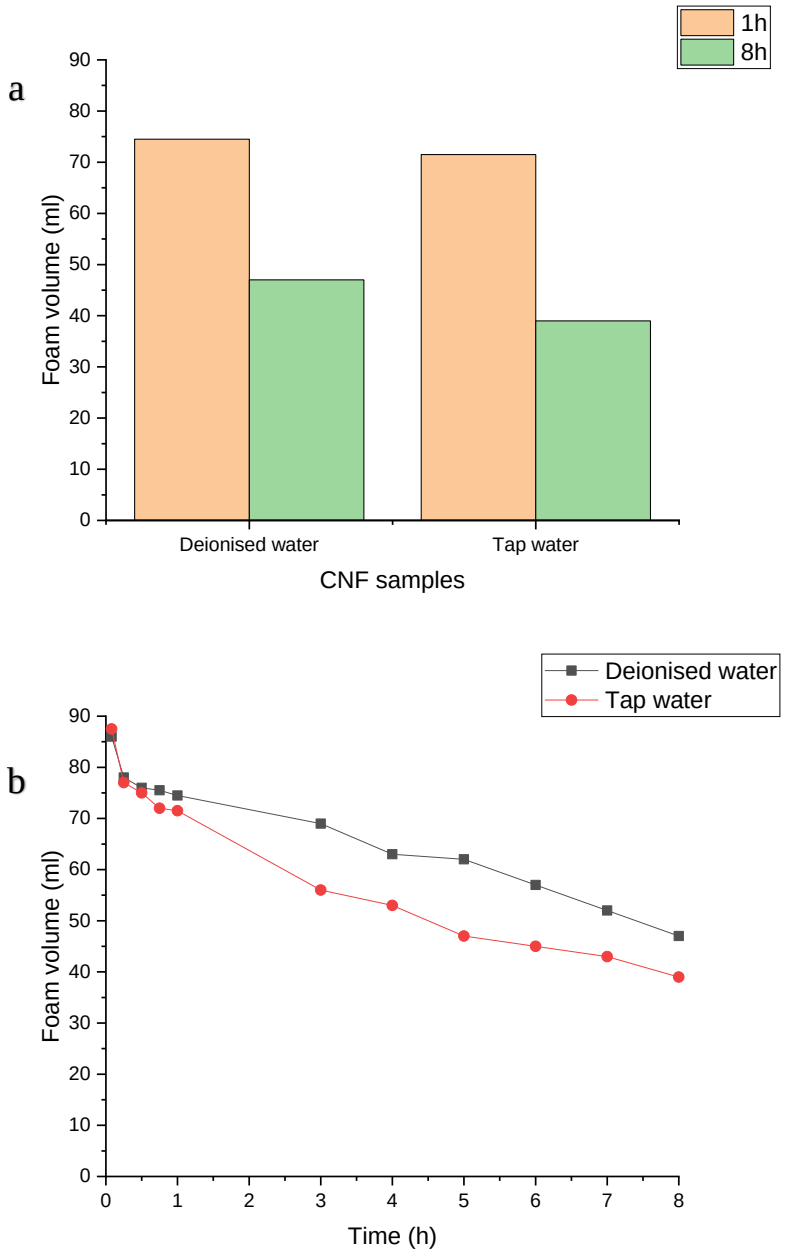

Figure 9:Foamability of CNF dispersions; a) foam volume of CNF samples with different types of water at 1 and 8h after preparation time; b) time evolution of foam volumes of CNF samples for 8 h. All samples contained 0.058g CNF, 0.75g tween 80, and 25ml of water.

4.2 Foam stabilization by lignin

Lignin is another abundant natural polymer. Its utilization in certain foam applications could be of interest due to its natural brown colour. Figure 10a shows lignin foam in a graduated cylinder during the earlier hours after preparation. Figure 10b shows lignin clumps stuck to the walls of the cylinder after the lignin foam dried.

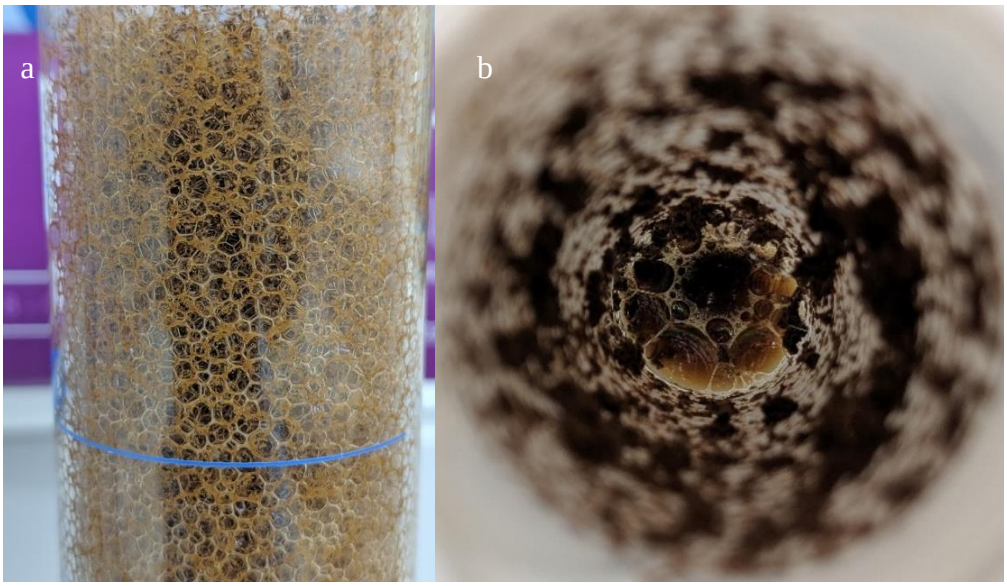

Figure 10: a) lignin foam; b) lignin residue on cylinder walls (top view).

Effects of lignin concentration on foamability are shown in Figure 11. Lignin foam degrades quickly, mainly due to the lack of fibrous structure, which gives plenty of support to the foams in cylinders as seen in the results for CNF shown above. Eventually, lignin foam dries and becomes very fragile, any movement of the cylinder could alter the volume of the foam. All samples contained 0.75 g Tween 80 and 25 ml deionised water.

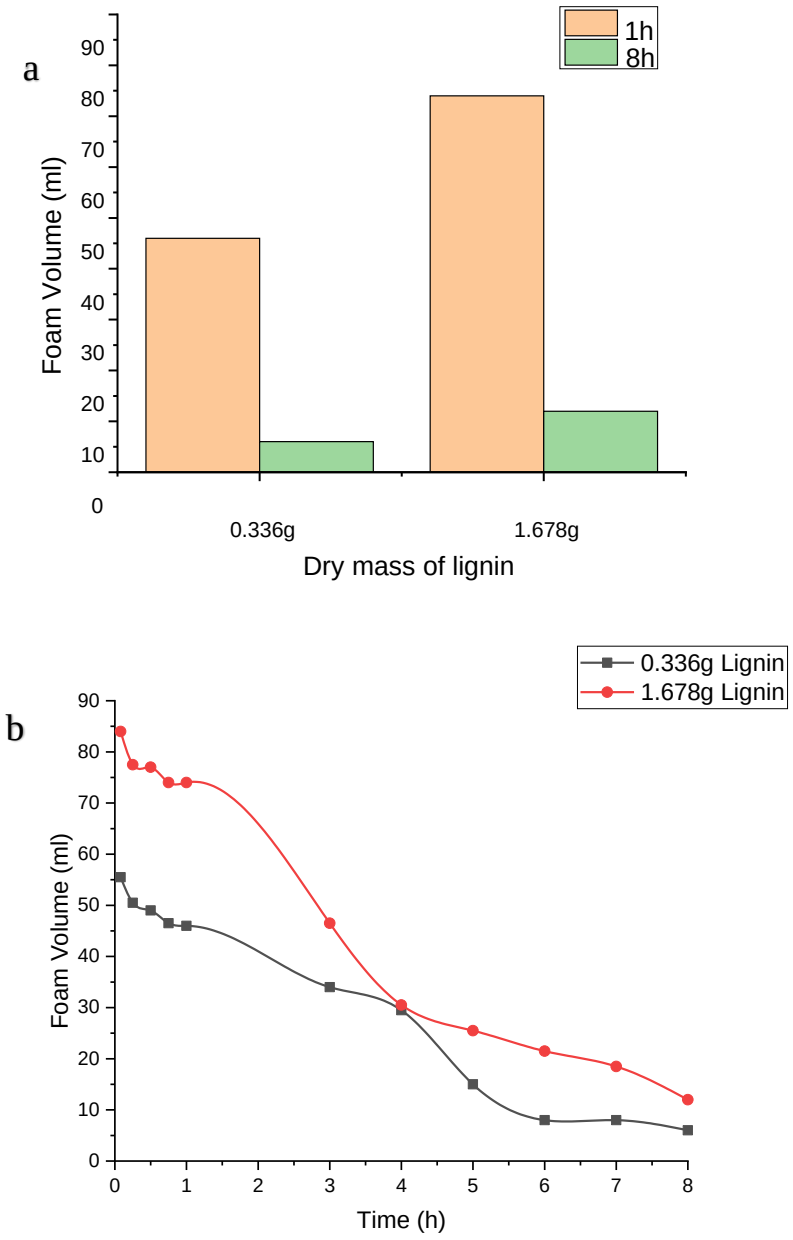

Figure 11: Foam volume of lignin dispersions; a) foam volume of lignin samples with different dry masses at 1 and 8h after preparation; b) time evolution of foam volume of lignin samples. All the samples contained 0.75 g Tween 80, and 25 ml deionised water.

The effect of surfactant type and concentration on the lignin foams is shown in Figure 12. Figure 12a shows five samples of lignin with Tween 80 and SDS compared after 1 and 6 h of preparation time, whereas Figure 12b shows the same samples foam volumes over 6 h. All samples contained dry weight of 1.678 g lignin and 25 ml deionised water. The SDS samples show very similar results, and the differences decrease later through the experiment. While the 0.75 g Tween 80 sample has shown similar results to the SDS samples initially, it is less stable

and degrades faster after the 3rd h. The 0.15 g Tween 80 samples shows less foamability and stability, so a higher concentration of Tween 80 is essential for a stable foam. For SDS, this shows that a lower concentration can be used for similar results.

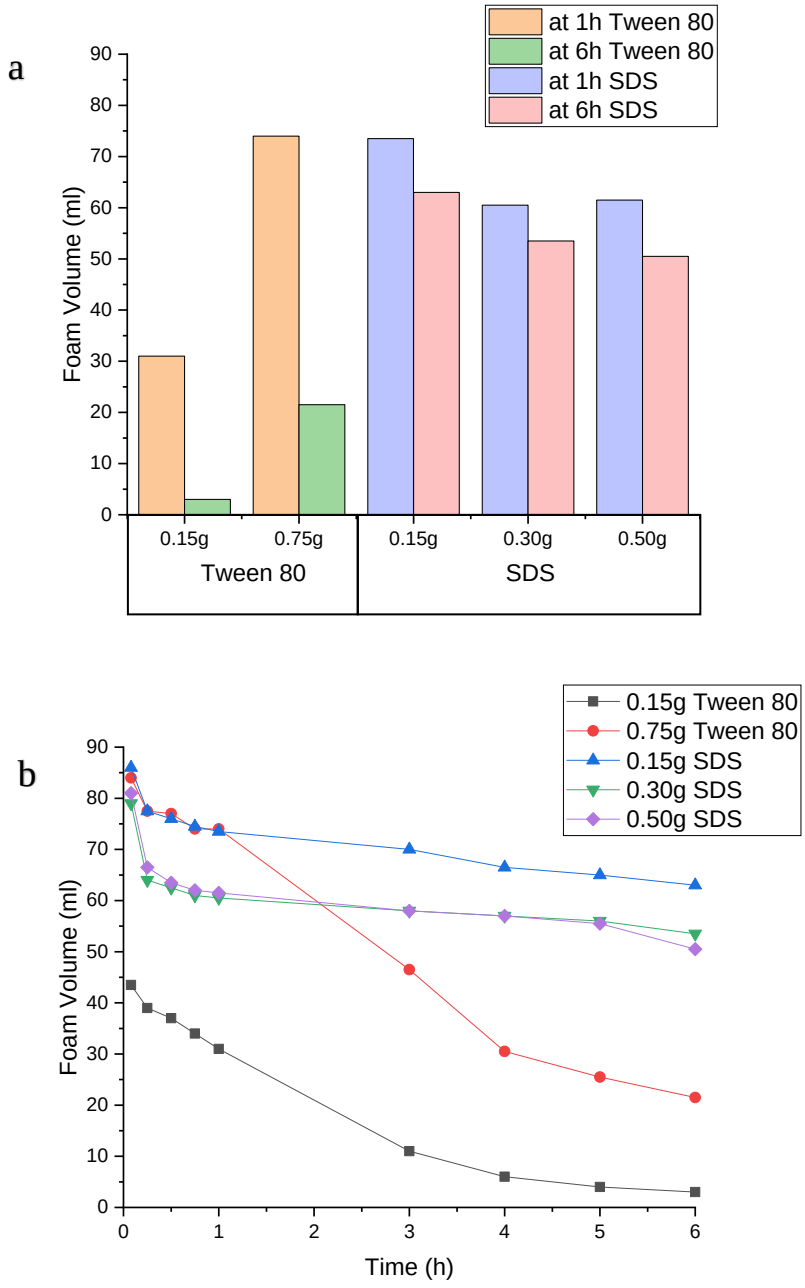

Figure 12: Foam volume of lignin dispersions; a) foam volume of lignin samples with different Tween 80 and SDS concentrations at 1 and 6 h after preparation. b) time evolution of foam volume of lignin samples. All the samples contained 1.678g lignin and 25ml deionised water.

4.2.1 Colloidal lignin particles

CLPs (Colloidal lignin particles) were tested as stabilizing particles for the foam instead of surfactants. CLPs foam readily, and with their amphiphilic nature, they were believed to create stable natural foams. 8ml of foam were created immediately during mixing the sample, however, the foam disappeared soon afterwards. This showed that CLPs are not suitable for stabilizing foams. Figure 13 shows prepared CLPs, before being concentrated further. Also, their distinctive light brown colour is shown. Even when CLPs create foam easily without mixing, they are not suitable for foaming.

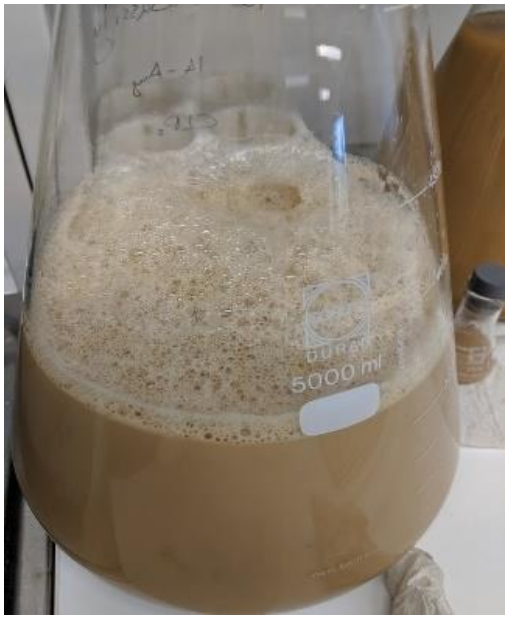

Figure 13: CLPs in a flask

4.3 Foam stabilization by CNF and lignin

CNF and lignin were combined in order to obtain the CNF's stability while retaining the colour of lignin. Three CNF+lignin samples are shown in Figure 14 after preparation.

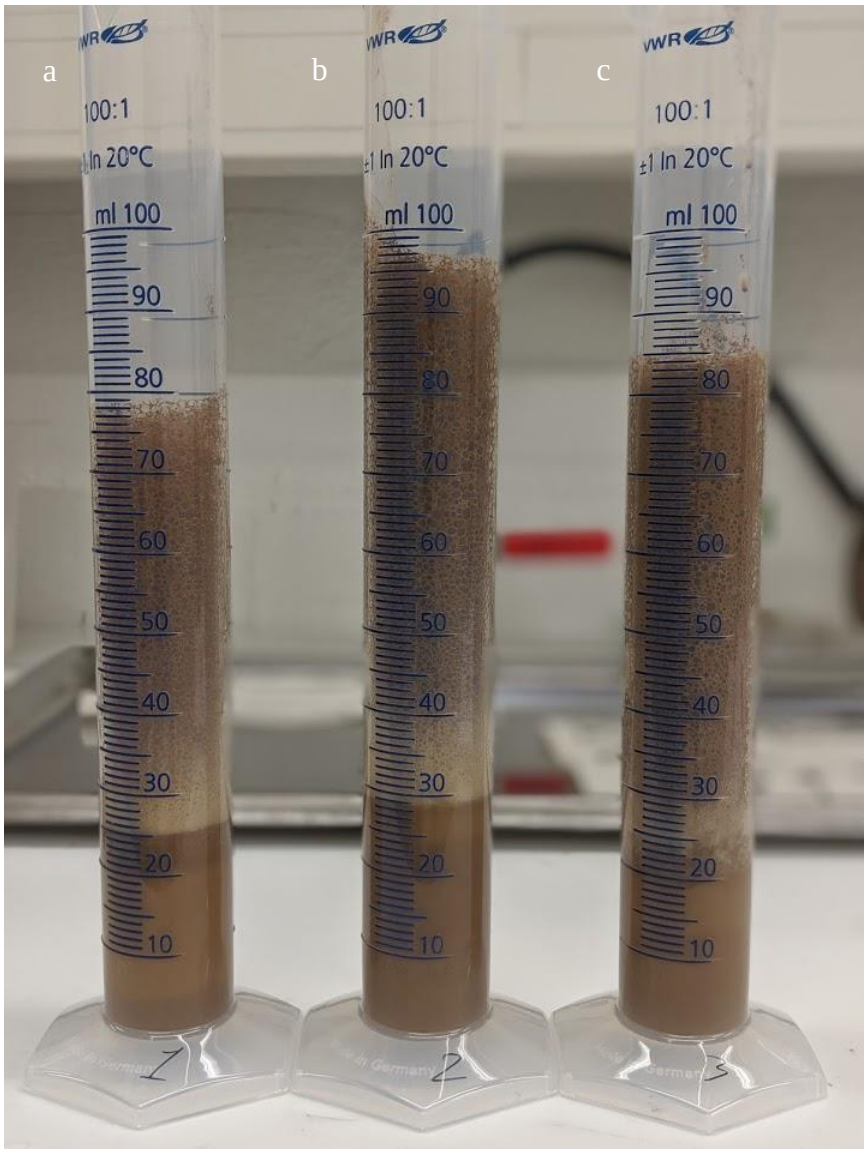

Figure 14: Foams from CNF+lignin dispersions with different quantities of each material: Sample a) CNF (0.029 g) and lignin (0.839 g); sample b) CNF (0.058 g) and lignin (2.684 g); sample c) CNF (0.092 g) and lignin (1.678 g). All samples contained 0.75 g Tween 80 and 25 ml deionised water.

A control sample, containing 0 g of CNF and 1.678 g lignin, 0.75 g Tween 80, and 25 ml deionised water, was used to compare the effect of different CNF concentrations on the foamability and foam stability of CNF and lignin mixtures (Figure 15). Figure 15a shows four CNF and lignin samples with different CNF concentrations at 45 minutes and 8 h after preparation. Figure 15b shows the foam volume of the same samples over a period of 8 h. The 0g CNF sample showed very high foamability, yet low stability. After 8 h, the samples with

higher concentrations of CNF had higher foam volumes, showing that the presence of CNF increased the foam stability.

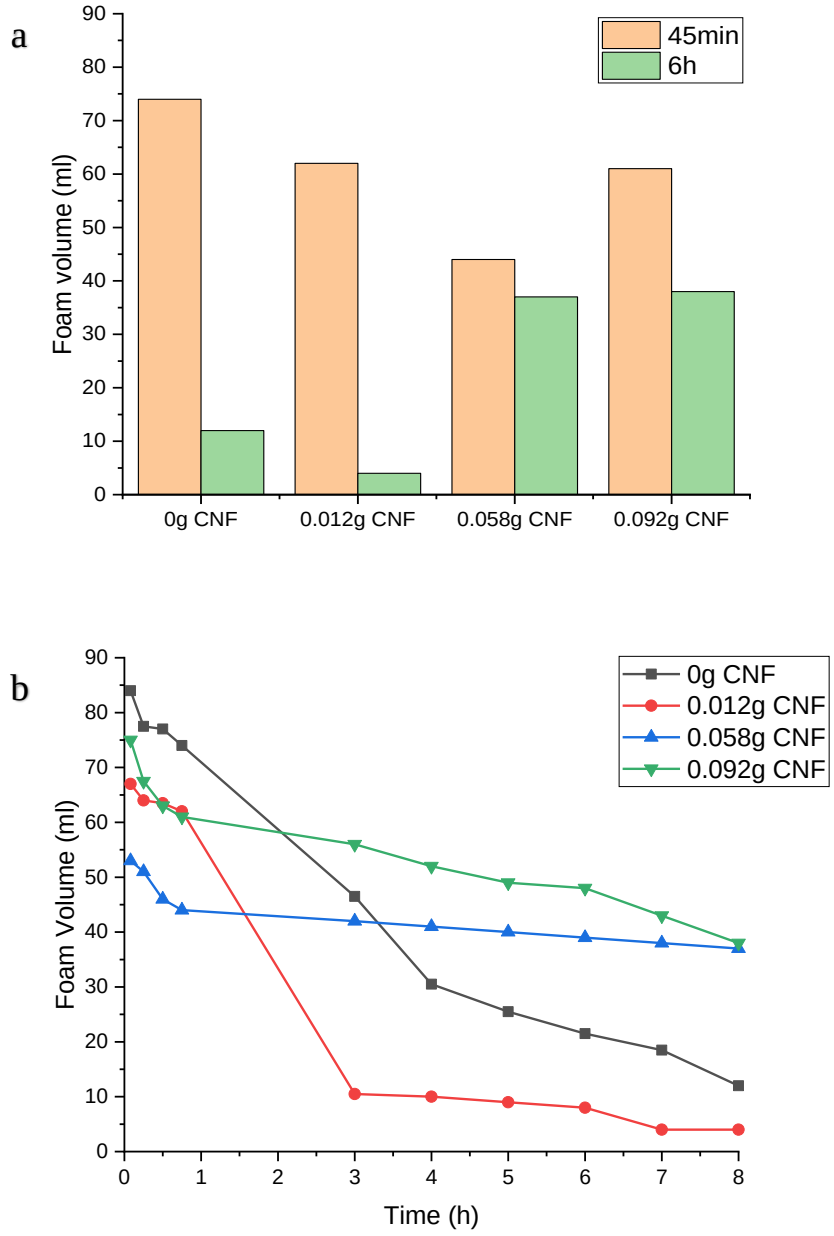

Figure 15: Foamability of CNF+lignin dispersions; a) foam volume of CNF+lignin samples with different CNF dry masses at 45 min and 8 h after preparation; b) time evolution of foam volume of CNF+lignin samples. All the samples contained 1.678 g lignin, 0.75 g Tween 80, and 25 ml deionised water.

The effect of the lignin concentration on the foam volumes and foam stability of CNF+lignin samples was also analysed. In Figure 16 four samples with various lignin concentrations are compared with one sample containing 0 g of lignin. All samples contained 0.058 g CNF, 0.75

g Tween 80, and 25 ml deionised water. Although there is some variability in the results, they suggest that higher amounts of lignin help to get more stable foams. Nevertheless, due to lack of a clear trend, firm conclusions cannot be drawn based on these results. However, lignin provides the natural brown colour.

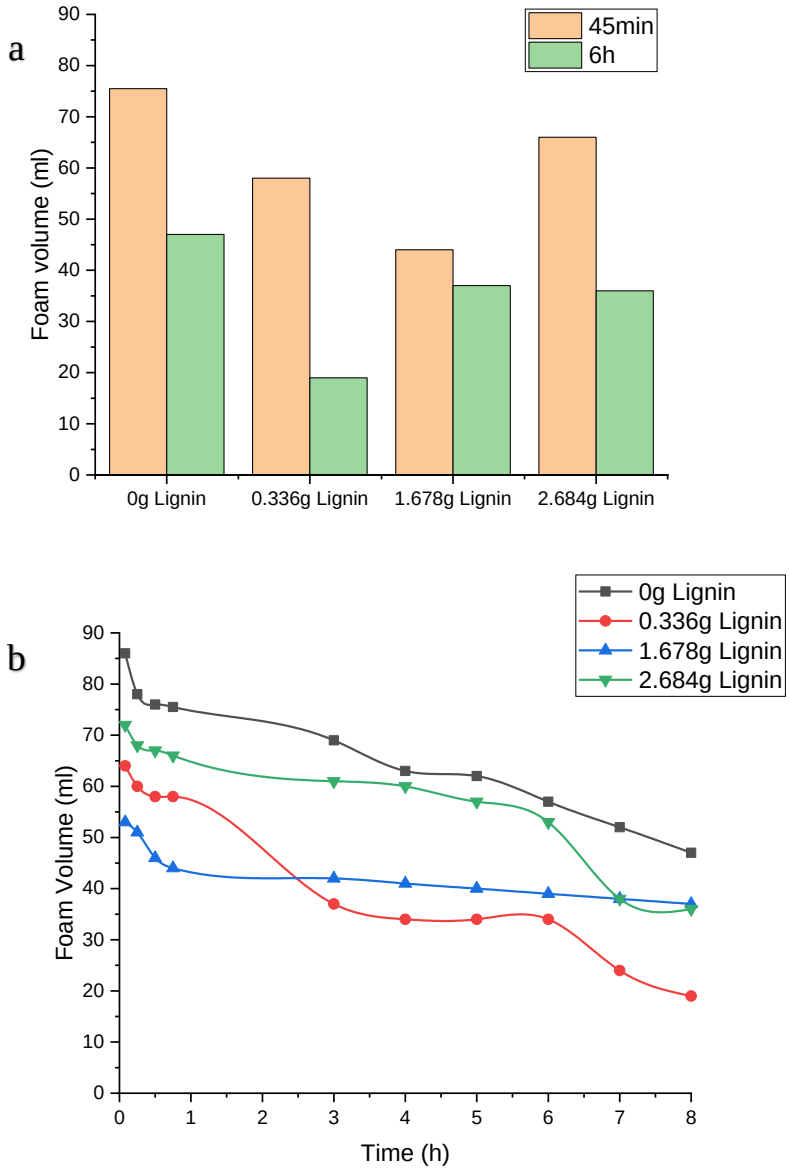

Figure 16: Foamability of CNF+lignin dispersions; a) foam volume of CNF+lignin samples with different lignin dry masses at 45 min and 8 h after preparation; b) time evolution of foam volume of CNF+lignin samples. All the samples contained 0.058 g CNF, 0.75 g Tween 80, and 25 ml deionised water.

The effect of surfactant type and concentration on the foamability of CNF and lignin dispersions are shown in Figure 17. All samples contained 0.058 g CNF and 1.678 g lignin dry

masses, and 25 ml deionised water. The 0.75 g Tween 80 sample behaved similarly to the SDS samples, all of which have high stability. The 0.15 g SDS sample had the highest foamability.

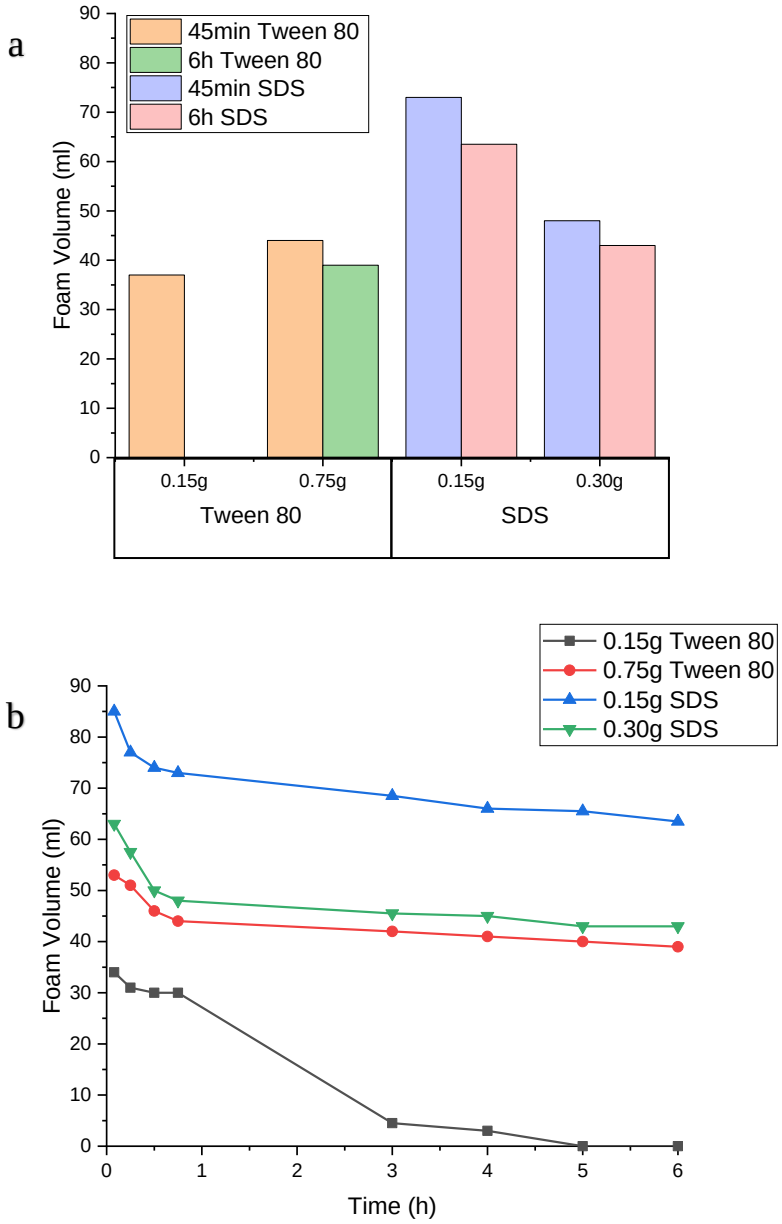

Figure 17: Foamability of CNF+lignin dispersions; a) foam volume of CNF+lignin samples with different surfactant types and concentrations at 45 min and 6 h after preparation; b) Time evolution of foam volume of CNF+lignin samples. All the samples contained 0.058 g CNF, 1.678 g lignin and 25 ml deionised water.

4.4 Foam stabilization by pulp

CNF is expensive to prepare. To find a cheaper solution, bleached and unbleached pulps were evaluated for stabilization of foams. Both were tested with Tween 80 and SDS. Bleached pulp

was less viscous than the unbleached pulp, and that helped in increasing the foam volume. The bleached fibres were most probably also more flexible than unbleached fibres. The unbleached pulp had long fibres that did not disperse easily and resulted in a highly viscous dispersion. There was difficulty in mixing the unbleached pulp using the homogeniser at hand due to its longer fibres and lower water content. Both pulps maintained their foam volumes for long periods of time in the graduated cylinders.

Figure 18a shows a bleached pulp sample with SDS surfactant. The image has backlighting to show the gaps and fibrous structure of the pulp foam. Figure 18b showed unbleached pulp foam, revealing the pulp structure and foam bubbles within. When both foams dried, the pulp retained the cylinders' shape and created a dry scaffold that can stay in the same shape for days.

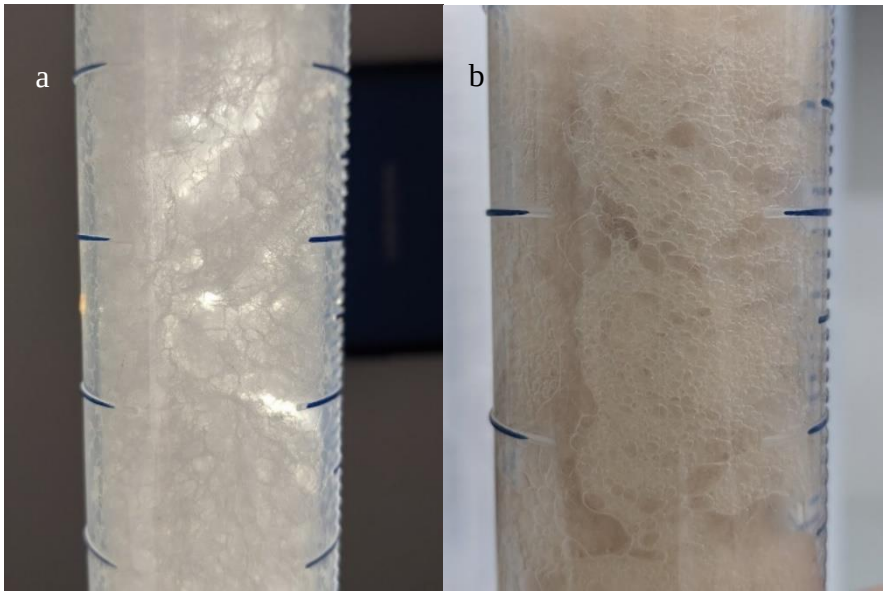

Figure 18: Foams from bleached and unbleadched pulps: a) 0.413 g bleached pulp with 0.15 g SDS (with backlighting); b) 0.412 g unbleached pulp with 0.75 g Tween 80.

The effect of the amount of bleached pulp on the foam formation and foam stability are represented in Figure 19 by comparing two bleached pulp samples with different dry masses. All samples contained 0.75 g Tween 80 and 25 ml deionised water, one sample contained 0.059 g bleached pulp and the other contained 0.413 g. While both samples had almost the same final foam volume after 24 h, the higher concentration of bleached pulp in the sample provided more support for the foam and made it much more stable, especially during the first 8 h. After 24 h, the foam is completely dry, and the remaining is a dry foam scaffold that relies on the pulp fibres for stability.

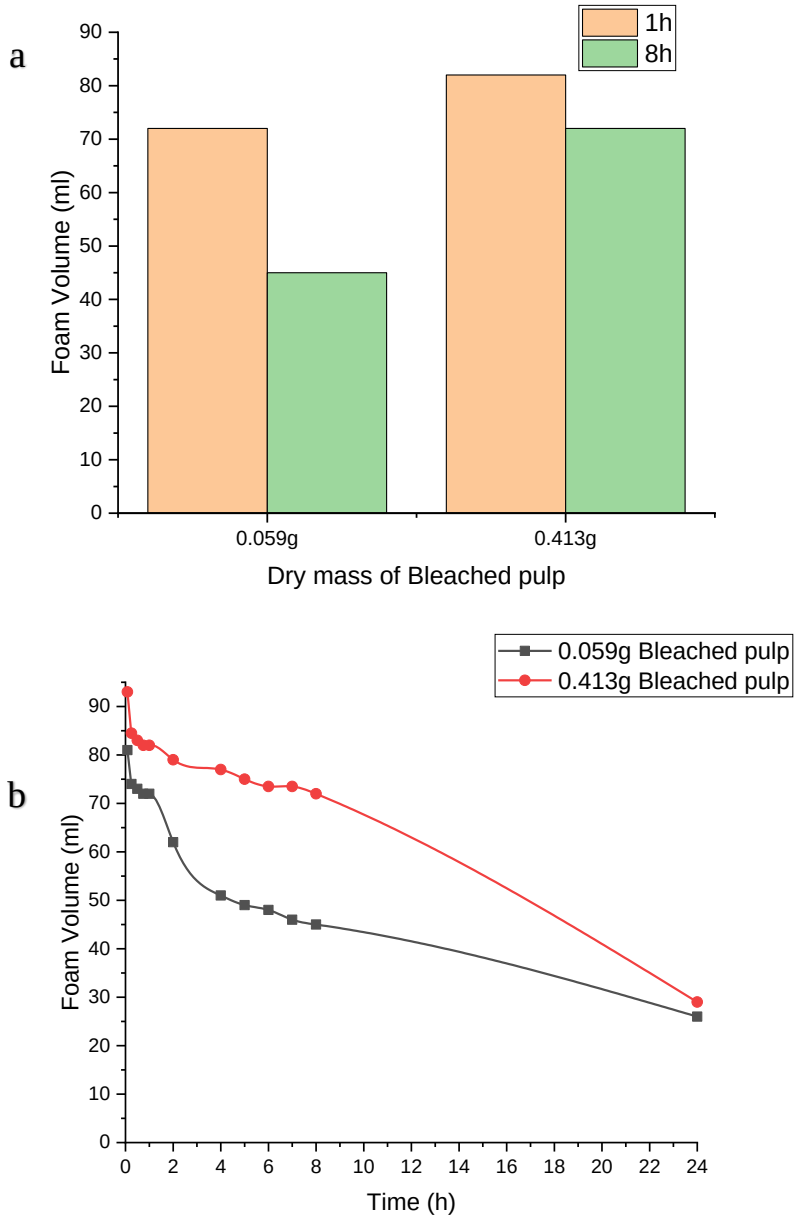

Figure 19: Foamability of bleached pulp dispersions; a) foam volume of bleached pulp samples with different dry masses at 1 and 8 h after preparation. b) time evolution of foam volume of bleached pulp samples. All samples contained 0.75 g Tween 80 and 25 ml deionised water.

The effect of the amount of unbleached pulp on the foam formation and foam stability are shown in Figure 20. All samples contained 0.75 g Tween 80 and 25 ml deionised water, while the unbleached pulp was changed in concentration. Three samples were tested, all provided a decent quantity of foam. The 0.058 g sample created the most volume of foam, but it was less stable than the other samples that contained higher concentrations of pulp. Increasing the amount of pulp provided the foams with more stability, but the dispersions were too viscous to create a large volume of foam.

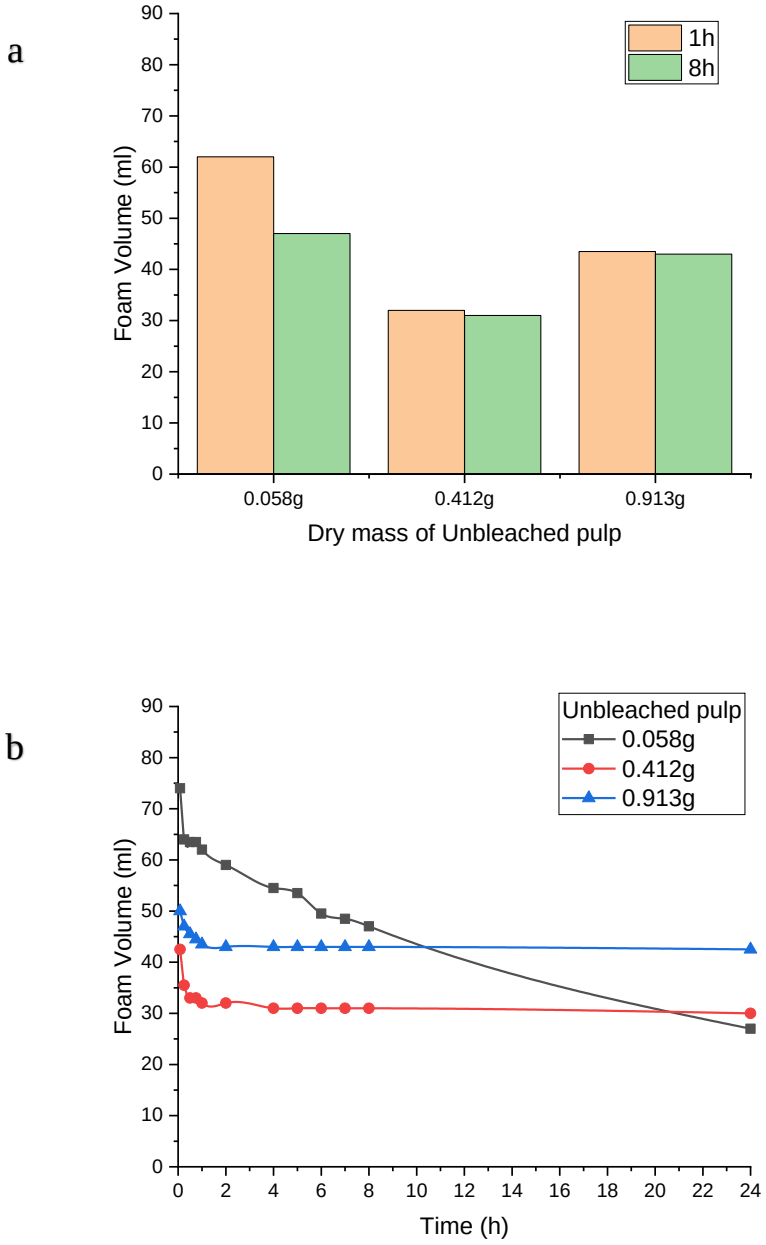

Figure 20: Foamability of unbleached pulp dispersions: a) foam volume of unbleached pulp samples with different dry masses at 1 and 8 h after preparation; b) time evolution of foam volume of unbleached pulp samples. All samples contained 0.75 g Tween 80 and 25 ml deionised water.

The effect of surfactant type and concentration on bleached pulp dispersions are shown in Figure 21. All samples contained 0.413 g bleached pulp and 25 ml deionised water. Figure 21a compared the samples at 1 and 8 h since preparation time. Both samples showed very similar results and great stability. The Tween 80 sample showed slightly larger volume of foam during the first 8 h of the experiment. Figure 21b showed the same samples, comparing the foam volume over the period of 24 h. Both samples showed great stability and the Tween 80 samples

had higher foam volume during the first 8 h. However, after 24 h, the Tween 80 sample degraded much faster, while the SDS sample remained stable throughout the experiment.

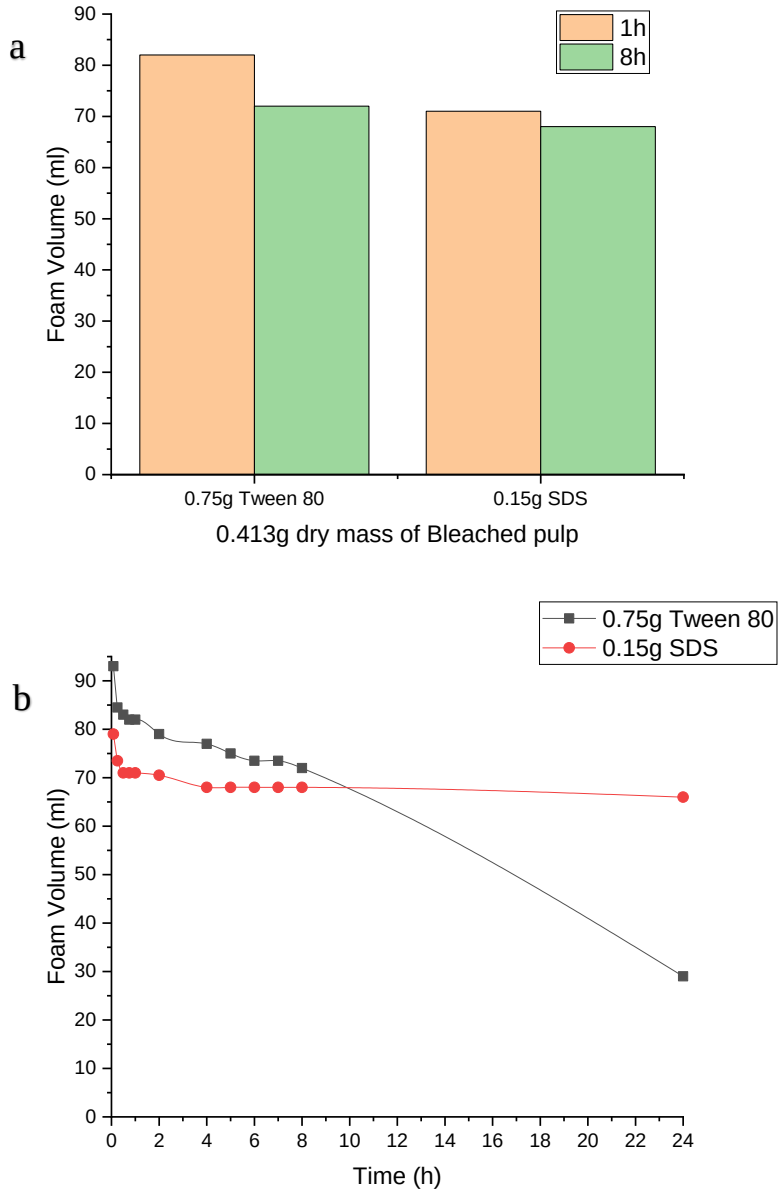

Figure 21: Foamability of bleached pulp dispersions; a) foam volume of bleached pulp samples with dry masses at 1 and 8 h after preparation; b) time evolution of foam volume of bleached pulp samples. All samples contained 0.413 g bleached pulp and 25 ml deionised water.

Two unbleached pulp samples with different concentrations of SDS are shown in Figure 22. Both samples contain 0.183 g of dry mass unbleached pulp and 25 ml deionised water. The sample with 0.07 g SDS showed higher foamability and decent stability. However, after 8 h, it degraded and reached 0 ml of foam after 24 h. In contrast, the foam volume of unbleached pulp

with 0.15 g SDS remained constant throughout the whole experiment, albeit the lower initial foam volume.

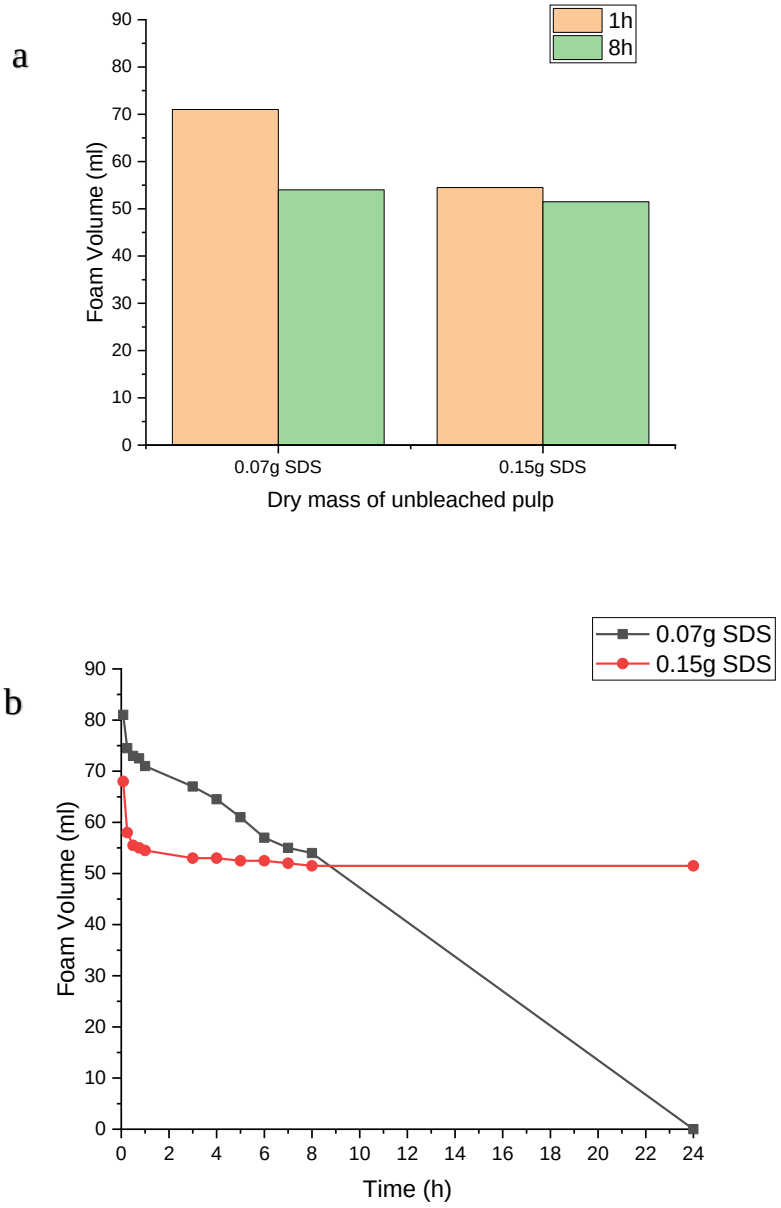

Figure 22: Foamability of unbleached pulp dispersions; a) foam volume of unbleached pulp samples with different concentrations of SDS at 1 and 8 h after preparation; b) time evolution of foam volume of unbleached pulp samples. All samples contained 0.183 g unbleached pulp and 25 ml deionised water.

Foam volume and foam stability obtained with different cellulose samples: CNF, bleached pulp, and unbleached pulp were all compared as shown in Figure 23. All samples contained the same dry mass of their respective material (~0.058 g), and they all contained 0.75 g Tween 80 and 25 ml deionised water. In other experiments (Figure 21), bleached pulp has proven to

remain the most stable over 24 h. As this experiment is limited to 8 h, the stability of the bleached pulp is not as evident. The CNF sample has shown better foamability initially, but ended up at the same level with the other samples, all resulting in very similar final foam volumes. For practical applications, pulp would be cheaper to produce and suitable for foam forming. CNF requires further fibrillation of the pulp, which requires energy and suitable equipment.

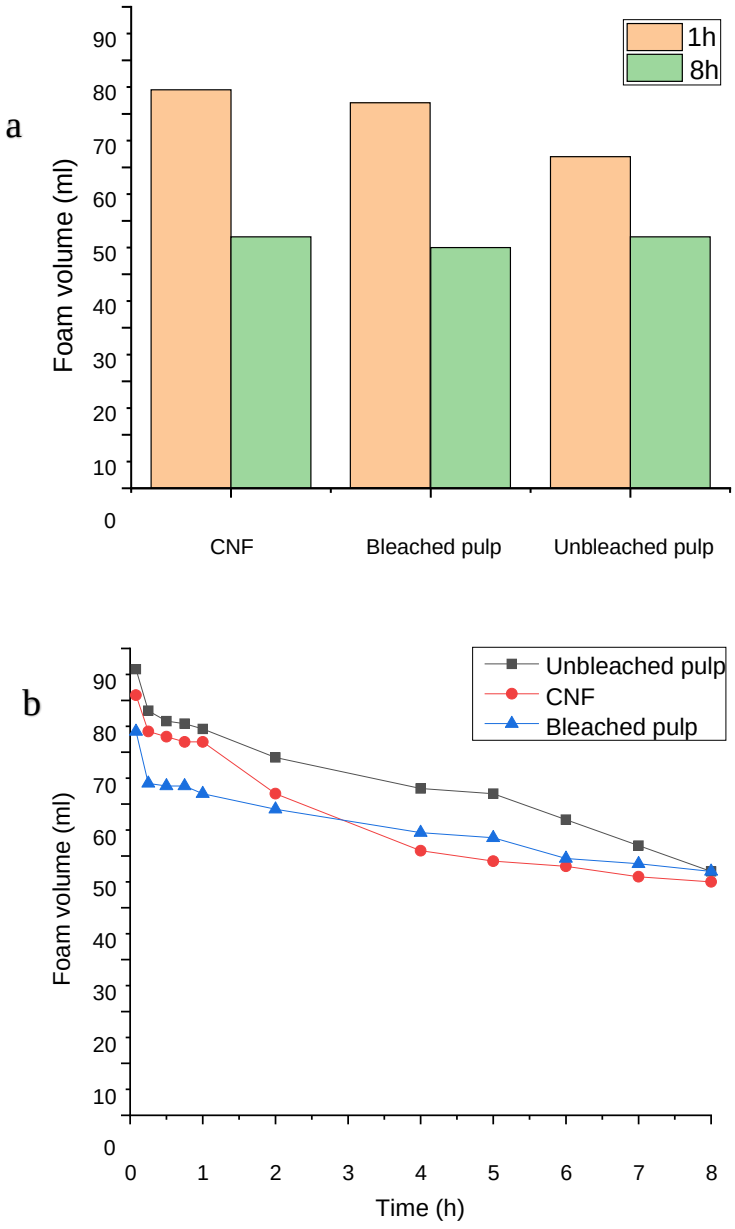

Figure 23: Foamability of CNF, bleached and unbleached pulps dispersions; a) foam volume of CNF (0.058 g), bleached (0.059 g), and unbleached pulps (0.058 g) with similar dry masses at 1 and 8 h after preparation; b) time evolution of foam volume for CNF, bleached, and unbleached pulps with similar concentrations. All samples contain 0.75 g Tween 80 and 25 ml deionised water.

4.5 Foam stabilization by pulp and lignin

Lignin was combined with pulp in order to get foams with the natural brown colour that wood has. The effect of surfactant type and concentration on bleached pulp and lignin dispersions are shown in Figure 24. All samples contained 0.413 g bleached pulp and 25 ml deionised water. Figure 24a shows two samples with different surfactants used, Tween 80 and SDS, compared at 1 and 8 h after preparation time. Figure 24b shows the foam volume against time for 24 h. The SDS sample produced more foam, but both samples were quite stable throughout the whole experiment.

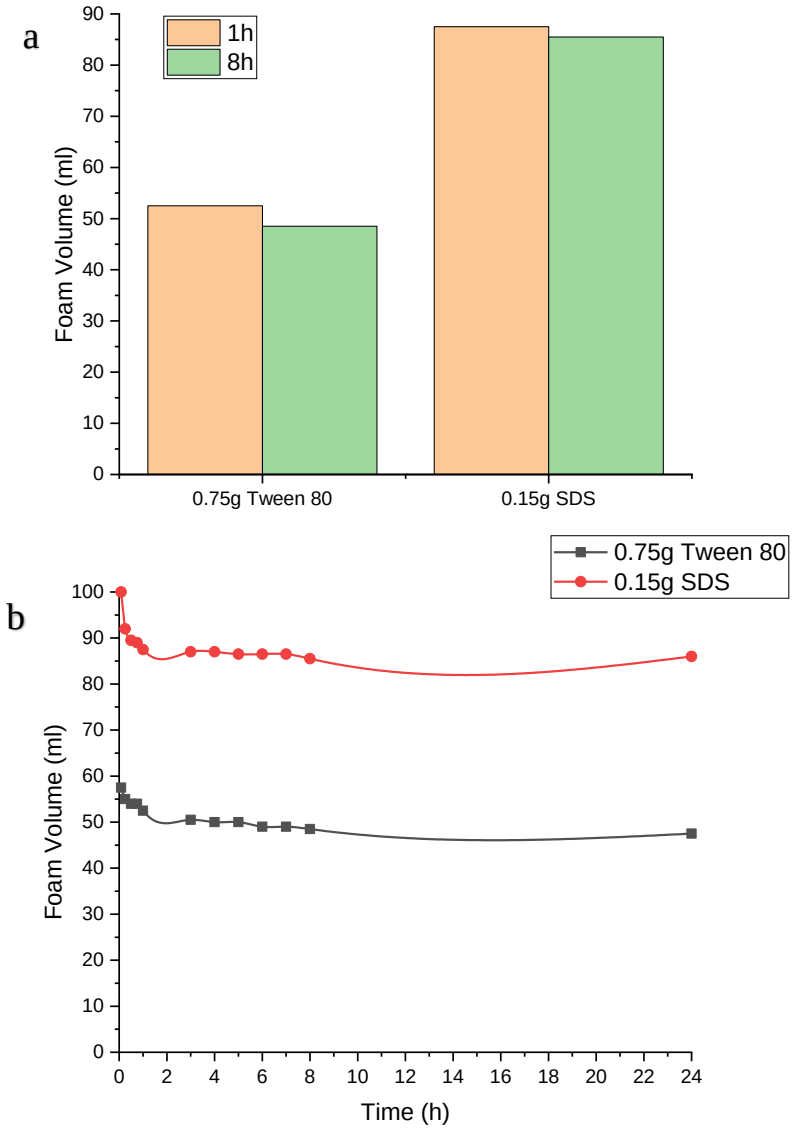

Figure 24: Foamability of bleached pulp and lignin dispersions: a) foam volume of bleached pulp and lignin samples with different surfactants at 1 and 8 h after preparation; b) time evolution of foam volume of bleached pulp and lignin samples. All samples contained 0.413 g bleached pulp and 25 ml deionised water.

The effect of surfactant type and concentration on CNF and lignin dispersions are shown in Figure 25, where two unbleached pulp and lignin dispersions are compared. Each sample was mixed with a different surfactant. Figure 25a shows the foam volume of both samples at 1 and 8 h after preparation time. Figure 25b shows the foam volume against time over 24 h. The SDS sample shows much better stability, however, both samples had a very high initial foam volume.

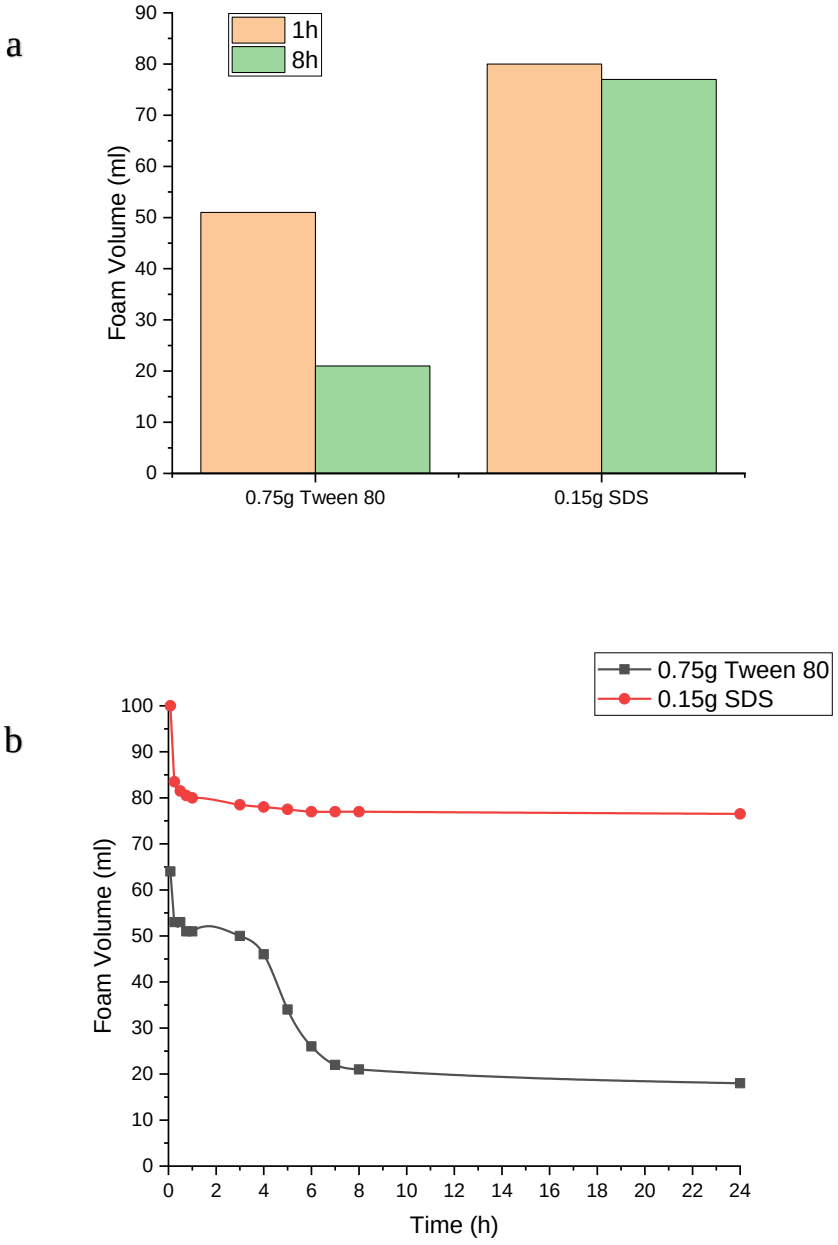

Figure 25: Foamability of unbleached pulp and lignin dispersions; a) foam volume of unbleached pulp and lignin samples with different surfactants at 1 and 8 h after preparation; b) time evolution of foam volume of unbleached pulp and lignin samples. All samples contained 0.183 g unbleached pulp and 25 ml deionised water.

A comparison of foam volumes for bleached pulp samples with and without lignin, and with different surfactants (Tween 80 or SDS), is presented in Figure 26. All samples contained dry mass of 0.413 g bleached pulp and 25 ml deionised water. The bleached pulp and lignin sample with SDS appeared to be the most stable throughout the whole experiment. Also, the SDS samples were generally more stable than the Tween 80 samples.

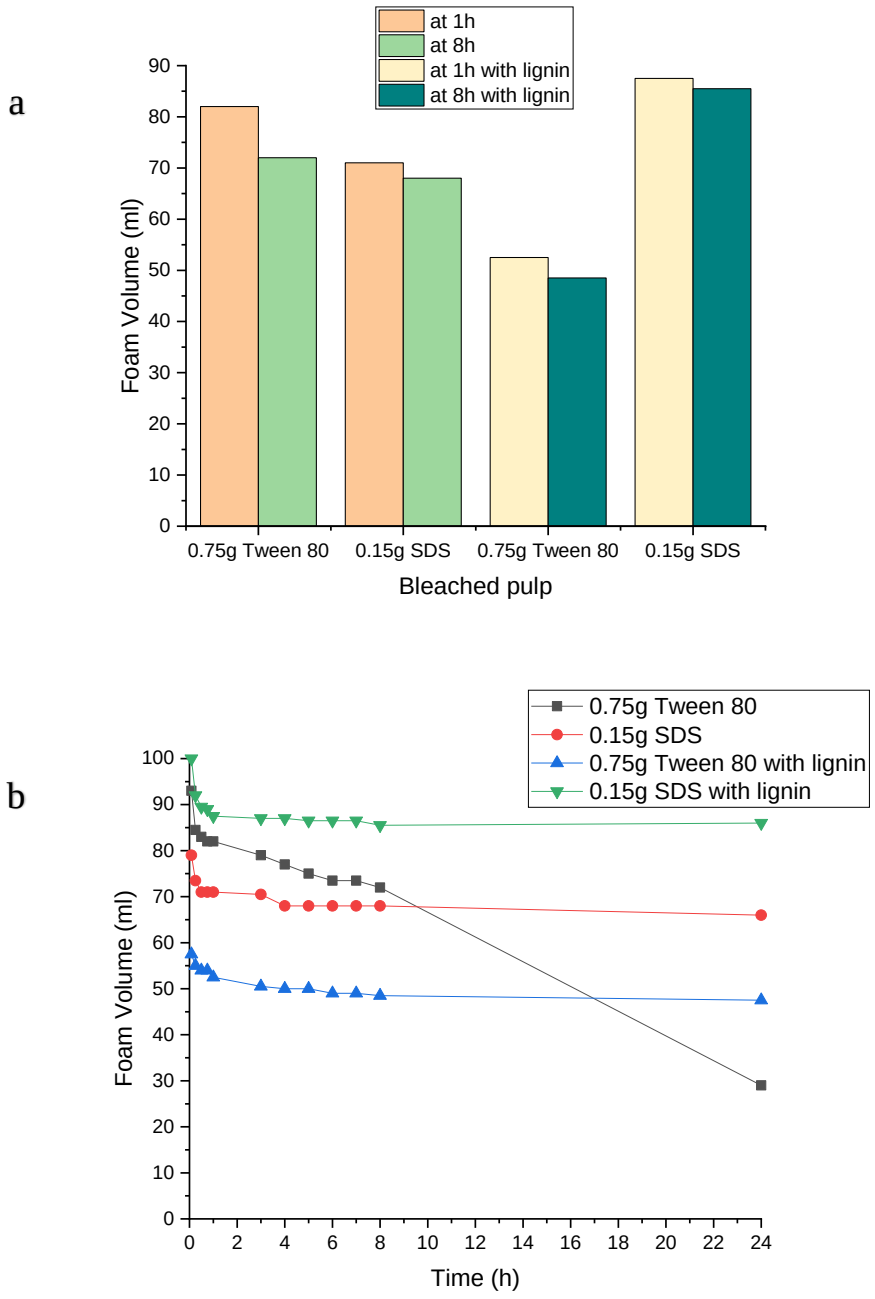

Figure 26: Foamability of bleached pulp and lignin dispersions; a) foam volume of bleached pulp and lignin samples with different surfactants at 1 and 8 h after preparation, compared to lignin-free samples; b) time evolution of foam volume of bleached pulp and lignin samples. All samples contained 0.413 g bleached pulp and 25 ml deionised water.

The effect of surfactant type and concentration on unbleached pulp and lignin dispersions are shown in Figure 27. Three unbleached pulp samples were compared, two of which contained lignin with different surfactants, and one mixed with SDS is without lignin. All samples contained 0.183 g unbleached pulp and 25 ml deionised water. This concentration of unbleached pulp was chosen due to its high density and long fibres, decreasing the mass in the samples allowed for better mixing using the homogeniser.

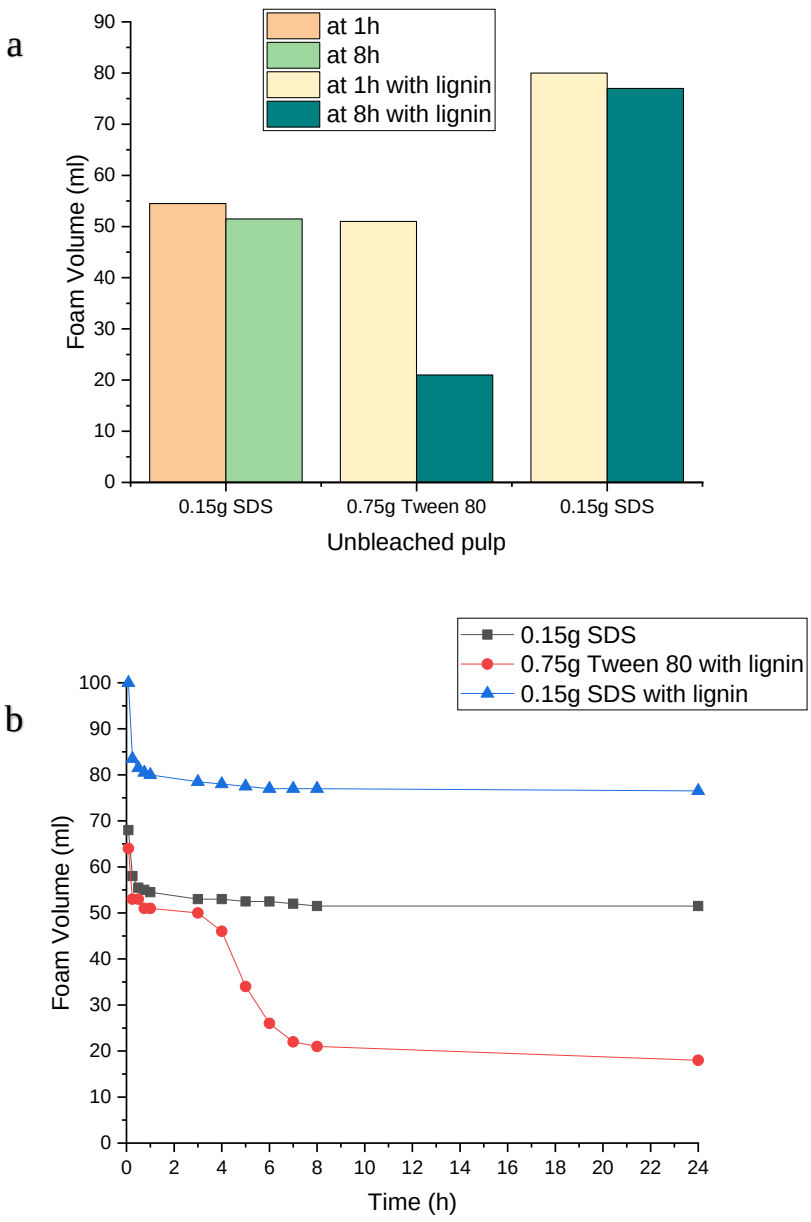

Figure 27: Foamability of unbleached pulp and lignin dispersion; a) foam volume of unbleached pulp and lignin samples with different surfactants at 1 and 8 h after preparation, compared to lignin-free samples; b) time evolution of foam volume of unbleached pulp and lignin samples. All samples contained 0.183 g unbleached pulp and 25 ml deionised water.

The unbleached pulp sample with the Tween 80 has the lowest stability, the SDS samples are much more stable. The SDS sample with lignin proved to be the most stable out of the three showing that lignin may act as a co-surfactant.

4.5.1 Cationic lignin

Cationic lignin was tried as a replacement for the surfactants used previously. Due to the limited quantity, it was tested with bleached pulp only. The colour is darker than kraft lignin. The dry weight of the cationic lignin was 0.75 g, while the bleached pulp was 0.413 g dry weight. The only other addition was deionised water to complete the total volume of water up to 25 ml – the cationic lignin was in solution.

Figure 28 shows a top view of the bleached pulp remaining stuck to the walls of the graduated cylinder after the foam dried out, and the dark colour at the bottom is cationic lignin solution.

Figure 28: Pulp traces stuck to the walls of the cylinder after the foam dried out

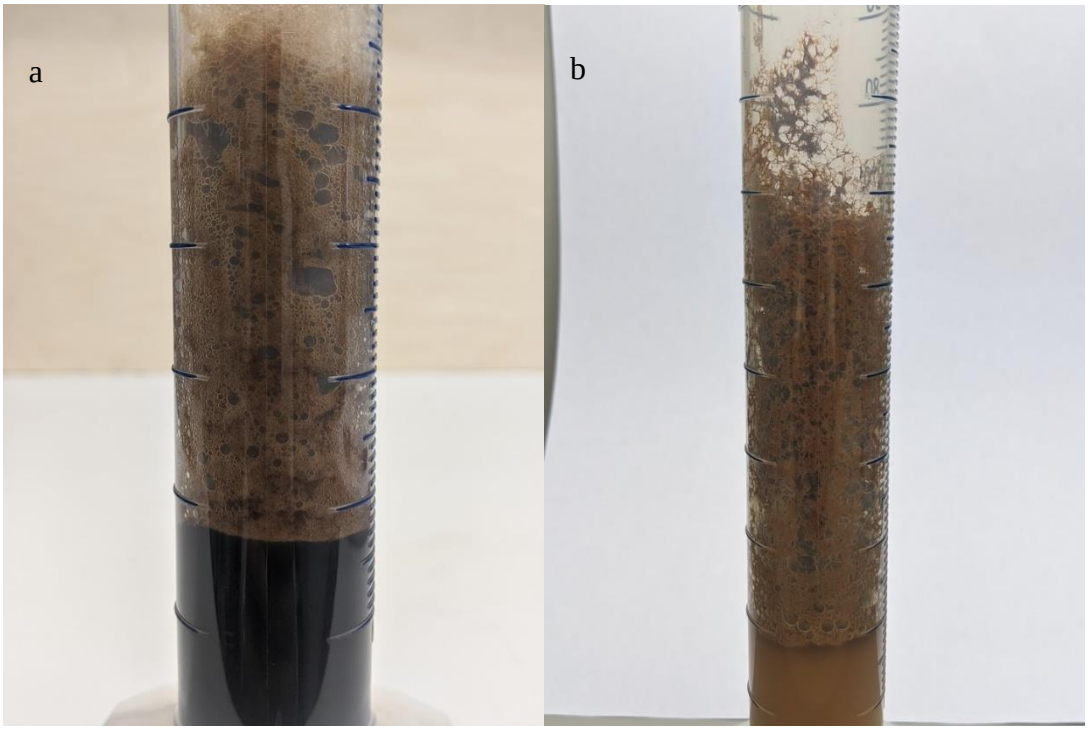

Figure 29: Foams formed by bleached pulp dispersions containing: a) 0.75 g cationic lignin; b) 1.678 g lignin and 0.75 g Tween 80 . All samples contained 0.413 g bleached pulp and 25 ml deionised water.

Two bleached pulp samples were prepared, one with cationic lignin shown in Figure 29a, and one with lignin and Tween 80 and is shown in Figure 29b. Both samples contained 0.413 g bleached pulp and 25 ml deionised water. Figure 29 compared kraft lignin with Tween 80 (Figure 29b) to a cationic lignin sample (Figure 29a). Cationic lignin is darker in colour compared to kraft lignin, and the difference is more prominent in the liquid section of the graduated cylinders. However, the difference in the foams' brown colour between both samples is less distinctive to the naked eye.

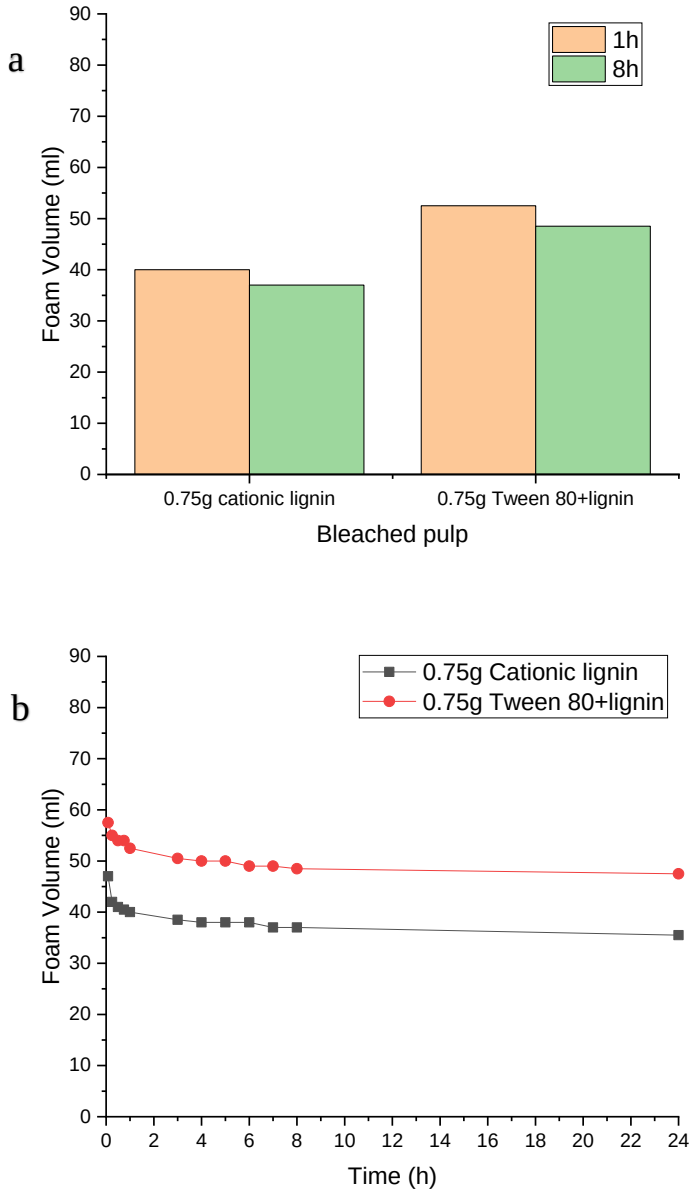

Figure 30: Foamability of bleached pulp dispersions; a) foam volume of bleached pulp samples with different surfactants at 1 and 8 h after preparation; b) time evolution of foam volume of bleached pulp samples. All samples contained 0.413 g bleached pulp and 25 ml deionised water.

The analysis of the foam stability of the samples shown in Figure 29 is presented in Figure 30. Both samples contained 0.413 g dry weight of bleached pulp, 25 ml deionised water, and 0.75 g of each surfactant or stabilizer; cationic lignin and Tween 80. Only the sample containing 0.75 g Tween 80 contained 1.678 g lignin. Figure 30a shows the foam volumes of both samples at 1 and 8 h, with little difference between both samples. While Figure 30b shows a similar trend between both samples, that is due to the stability of bleached pulp, with a little difference between Tween 80 and cationic lignin in terms of foamability. Cationic lignin is a competent foam stabilizer and is a valid alternative to surfactants.

4.6 Foam colouration using Chlorophyll

CNF and bleached pulp were combined with chlorophyll, separately, to provide the foams with green colour. Both CNF and bleached pulp had a bright white colour, which makes it easy to recolour. Chlorophyll was added to the samples to observe how effective it is as a colourant.

4.6.1 Pulp foam colouration

Bleached pulp samples were tested with different quantities of chlorophyll and different types of surfactants. The dry mass of chlorophyll was either 0.5 or 1 g. The surfactants used were Tween 80, SDS, and CTAB. CTAB, a cationic surfactant, was thought to help improve chlorophyll dispersion in the foam due to its charge. However, it is quite hazardous and cannot be used with these foams in practice – as one of the main objectives is to produce a completely natural foam (Santa Cruz Biotechnology, 2009). CTAB has been tested with a sample to show the effects of a cationic surfactant and whether it would be ideal to find a natural cationic surfactant for the foam, which was not available in the labs for testing.

Bleached pulp and chlorophyll dispersions have been prepared with CTAB and Tween 80 for comparison in Figure 31, the difference in colour was not visible to the naked eye.

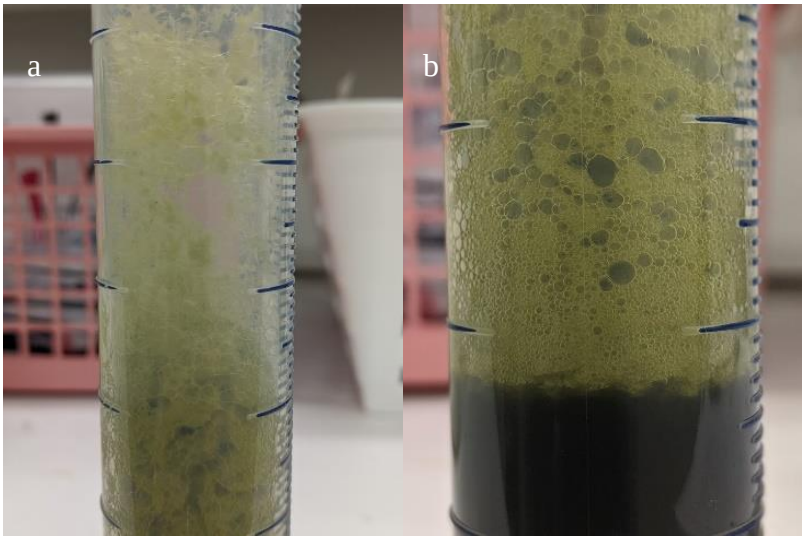

Figure 31: Foam formed by bleached pulp and chlorophyll dispersions with: a) 0.5 g CTAB; b) 0.75 g Tween 80. All samples contained 0.413 g bleached pulp and 25 ml deionised water.

The effect of surfactant type and concentration on the formation and stability of foams from bleached pulp and chlorophyll dispersions are shown in Figure 32. Two bleached pulp and chlorophyll samples are compared, both samples contained 1 g dry mass chlorophyll (in form of dried flakes), 0.413 g bleached pulp, and 25 ml deionised water. Each sample used a different surfactant: Tween 80 and SDS. Figure 32a shows the comparison of the foam volumes of both samples at 1 and 8 h after preparation time. While in Figure 32b, the foam volume over time is shown over 24 h. The sample containing SDS has shown to create more foam and maintain it for a longer period of time. The difference in foam volume between the samples is more drastic after 3 h. There was no visible difference regarding the colours of the samples when using different surfactants. Both surfactants resulted in having a higher concentration of the chlorophyll in the liquid section, rather than in the foam itself.

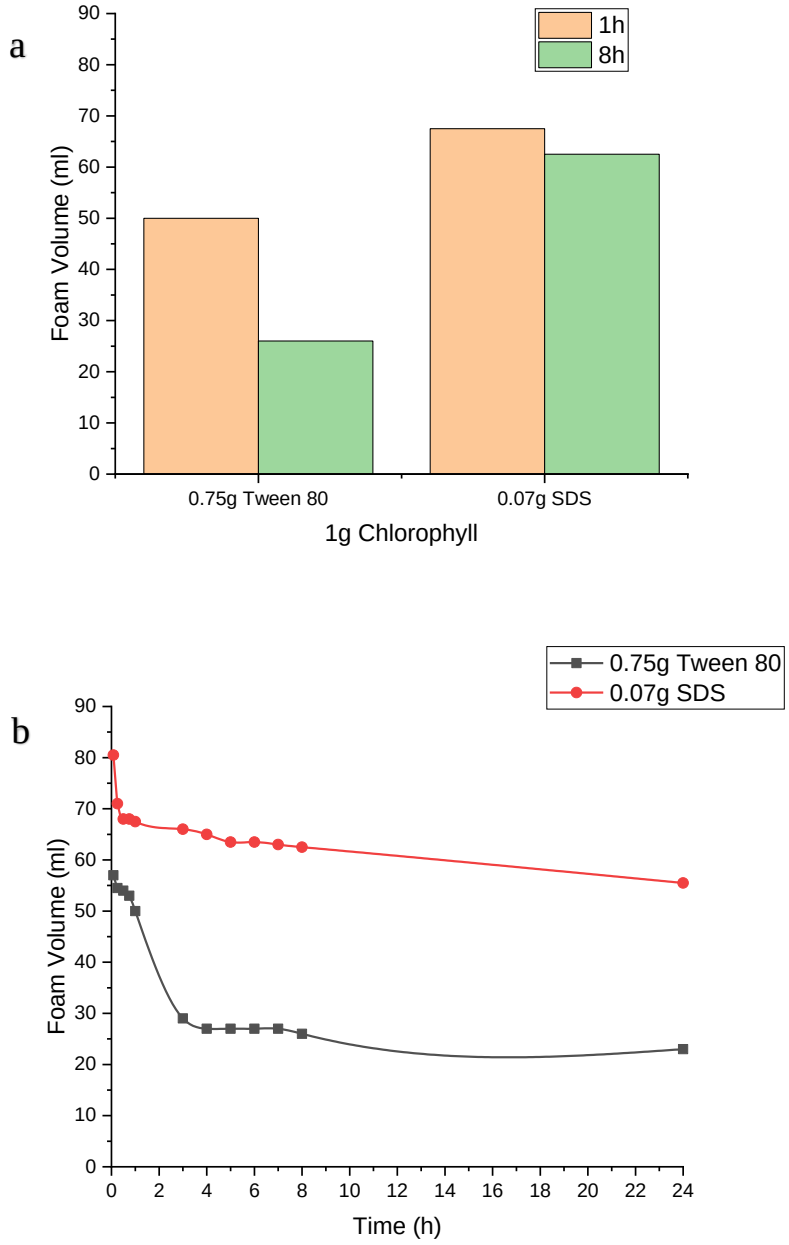

Figure 32: Foamability of bleached pulp and chlorophyll dispersions; a) foam volume of bleached pulp and 1 g chlorophyll samples with different surfactants at 1 and 8 h after preparation; b) time evolution of foam volume of bleached pulp and 1 g chlorophyll samples. All samples contained 0.413 g bleached pulp, 1 g chlorophyll, and 25 ml deionised water.

The effect of surfactant type and concentration on bleached pulp and chlorophyll dispersions are shown in Figure 33, where two bleached pulp and chlorophyll samples were compared. All samples contained 0.413 g dry weight of bleached pulp and 25 ml of deionised water, 0.5 g of dry chlorophyll and different surfactants: CTAB or Tween 80. CTAB is not a natural surfactant, in fact it is quite toxic. It has been used as it is a cationic surfactant and in theory should be able to increase the concentration of the chlorophyll in the foam rather than it escaping into the

liquid part. It was neither effective as a foaming agent nor as an option to increase the greeness of the foam.

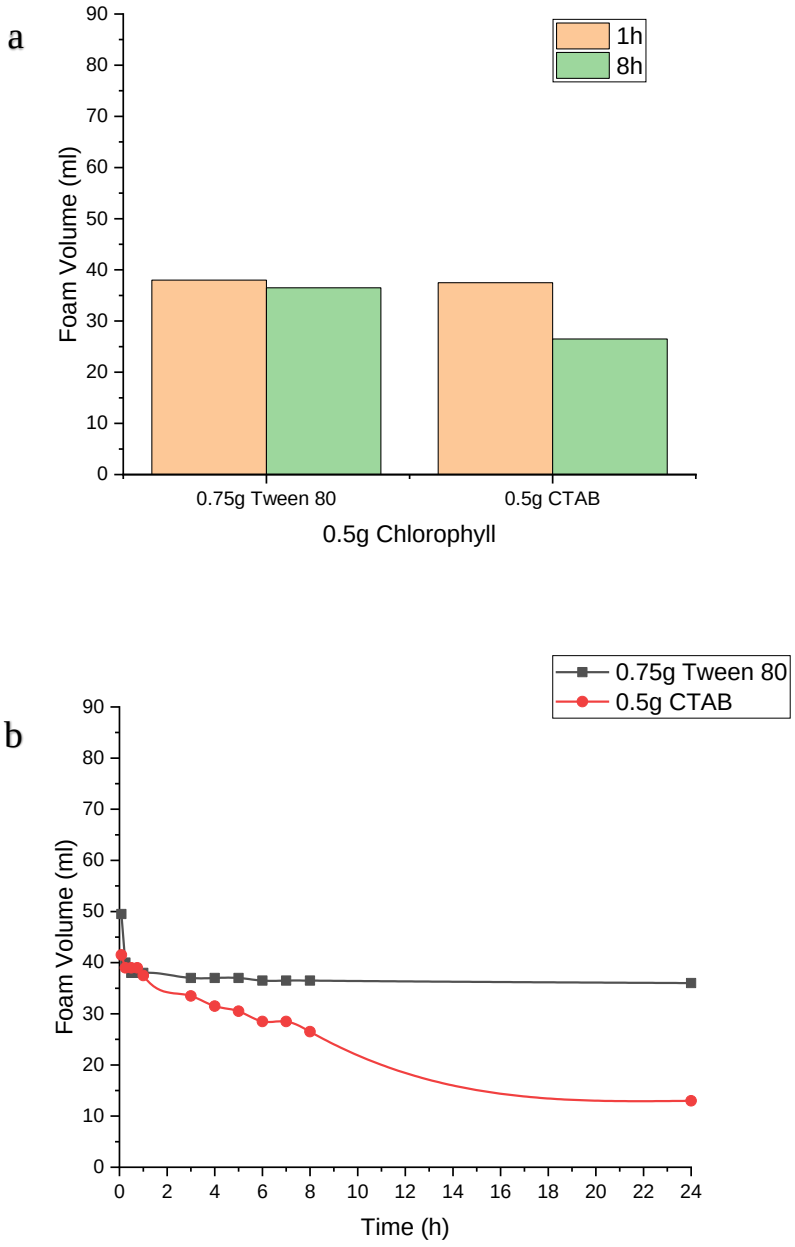

Figure 33: Foamability of bleached pulp and chlorophyll dispersions; a) foam volume of bleached pulp and 0.5 g chlorophyll samples with different surfactants at 1 and 8 h after preparation; b) time evolution of foam volume of bleached pulp and 0.5 g chlorophyll samples. All samples contained 0.413 g bleached pulp and 25 ml deionised water.

Three bleached pulp dispersions are compared in Figure 34, each with a different amount of chlorophyll. All samples contained 0.413 g bleached pulp, 0.75 g Tween 80, and 25 ml deionised water. The 0 g chlorophyll sample showed higher initial foam volume, that could

indicate that chlorophyll might affect the foamability. However, the stability does not appear to be affected, as after 24 h, all samples had similar foam volume.

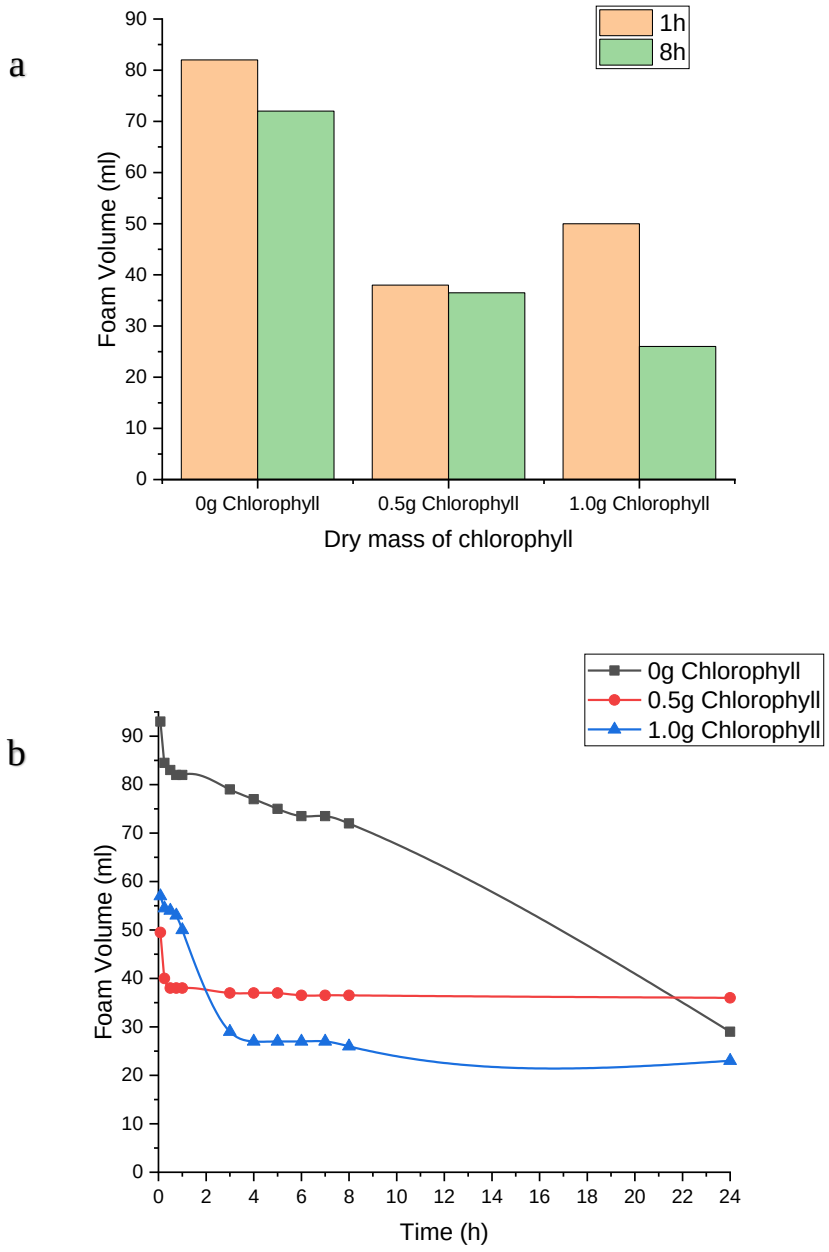

Figure 34: Foamability of bleached pulp and chlorophyll dispersions: a) foam volume of bleached pulp and chlorophyll samples with different chlorophyll dry masses at 1 and 8 h after preparation; b) time evolution of foam volume of bleached pulp and chlorophyll samples. All samples contained 0.413 g bleached pulp, 0.75 g Tween 80 and 25 ml deionised water.

The chlorophyll was mostly concentrated in the liquid part, due to its hydrophilicity, that resulted in a very light green colour in the foams. As shown in Figure 35, most of the

chlorophyll is concentrated in the liquid part and the foam is lighter than desired. The sample in Figure 35b contained 1 g dry chlorophyll, while the one in 35c contained 0.5 g chlorophyll.

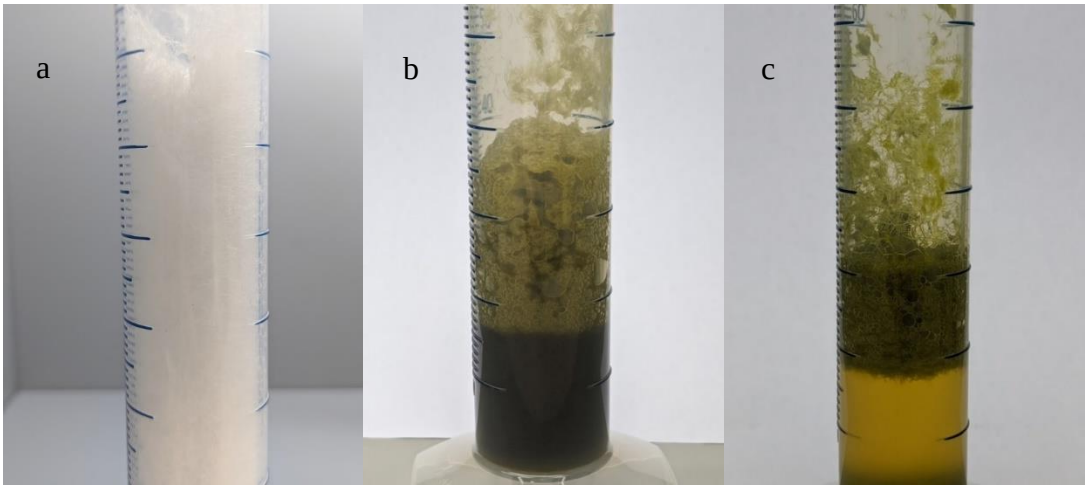

Figure 35: a) bleached pulp with Tween 80 – no chlorophyll; b) bleached pulp with Tween 80 and chlorophyll; c) bleached pulp with CTAB and chlorophyll.

Figure 35a shows bleached pulp sample with no chlorophyll, this is used as a reference to compare with the other samples. As shown in Figure 35c, the sample with CTAB has lower stability than the other samples, while the foam was light in colour and most of the pigmentation settled down. Figure 35b shows Tween 80 used instead of the CTAB, and it has a better appearance and high chlorophyll presence in the foam, as well as the better foam stability. This image was taken after 24 h had passed.

4.6.2 CNF foam colouration

CNF has been mixed with chlorophyll to observe how the dispersion would behave. In Figure 36, two CNF and chlorophyll samples are shown. Sample *a* contained 0.058 g CNF, 0.75 g Tween 80, 0.25 g dry mass chlorophyll, and 25 ml deionised water. Sample *b* contained 0.029 g CNF, 0.38 g Tween 80, 0.25 g dry mass chlorophyll, and 12.5 ml deionised water.

The main objective was to observe if higher concentration of chlorophyll would add a visible difference in colour density to the naked eye. Sample *b* was half of the size of sample *a* due to lack of prepared chlorophyll at hand, but both had similar ratios except of the chlorophyll concentration.

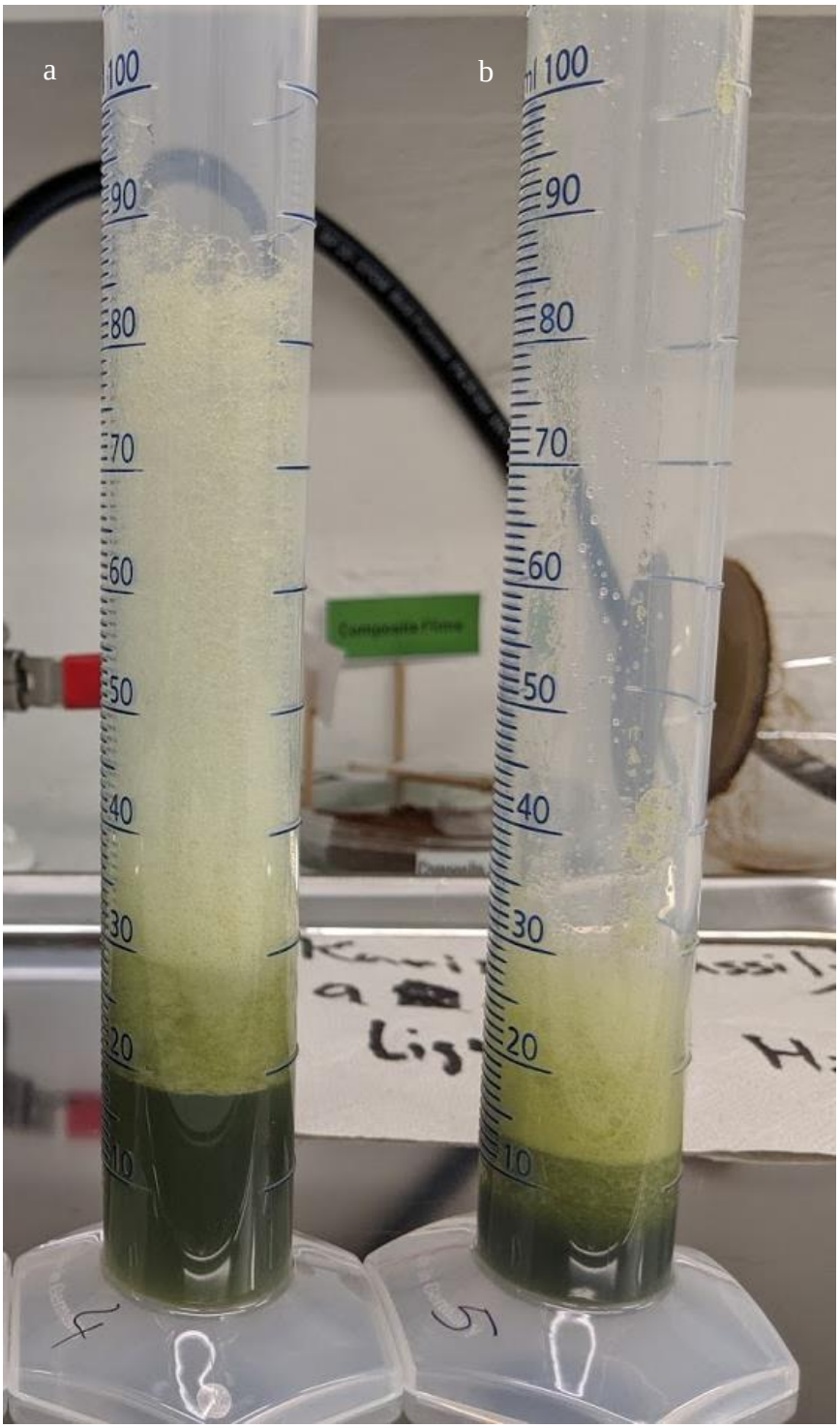

Figure 36: Foams from CNF and dry chlorophyll dispersions; a) foam dispersion of CNF (0.058 g), Tween 80 (0.75 g), and deionised water (25 ml); b) foam dispersion of CNF (0.029 g), Tween 80 (0.38 g), and deionised water (12.5 ml). All samples contained 12.5 g dry mass chlorophyll.

Due to the small sizes of the samples, the difference in colour was not clearly visible to the naked eye (Figure 36). Even with higher concentration of chlorophyll in sample *b*, the foam

appeared similarly pale to that of sample *a*. The CNF and chlorophyll samples were not very stable and by the end of the experiment neither had foam, as shown in Figure 37.

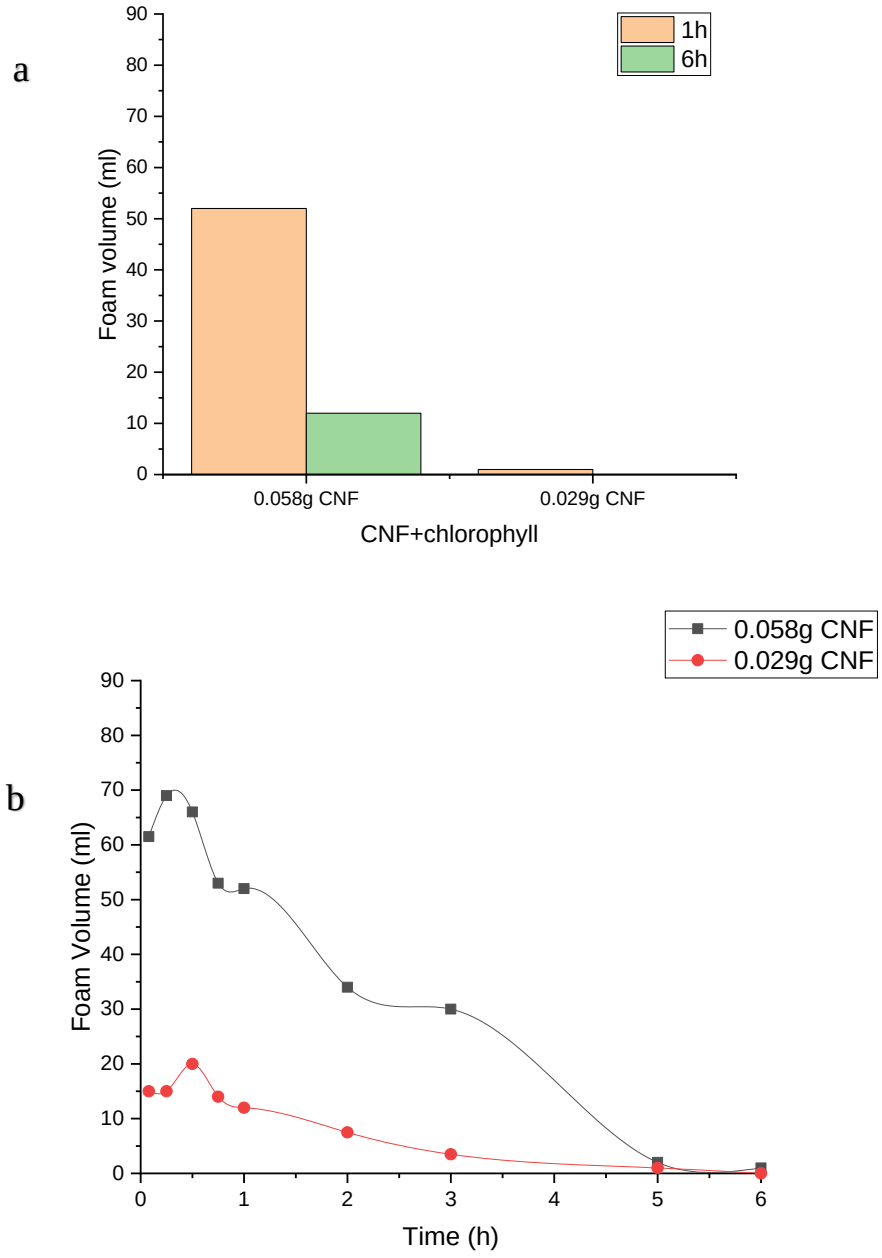

Figure 37: Foamability of CNF and dry chlorophyll dispersions: a) foam volume of CNF and chlorophyll samples with different sample sizes at 1 and 6 h after preparation; b) time evolution of foam volume of CNF and chlorophyll samples with different sample sizes. All samples contained 1.25 g chlorophyll.

5 Conclusions

Foams are essential for many applications, and there are plenty of industries relying on it. Replacing synthetic polymers with the natural counterparts will take years to achieve in many industries. However, in many niche applications, natural foams could be utilised fully.

In this thesis, natural foams were made using CNF, lignin, bleached and unbleached pulps, separately or combined. The foams were prepared by mixing those materials with surfactants and water using an IKA-Ultraturrax homogeniser. An increase in the foam stability was observed in some systems upon an increase in the amount of solid components. The pulps provided the highest stability for the foams, with the bleached pulps being the most stable out of all the natural polymers. That is probably due to their long fibres that can keep the foam volume stable for extended periods of time. When the foam dried out, the fibres formed a three-dimensional scaffold that attached to the walls of the graduated cylinders. SDS and Tween 80 were the two main surfactants used, and both provided high stability for the foams. SDS provided slightly higher stability at lower concentrations of surfactant.

Lignin and chlorophyll both contributed to the colour of the foams. The bleached pulp and CNF alone created a white foam, while the unbleached pulp created a light brown foam. Kraft lignin produced a dark brown foam, and when mixed with other components, it still retained that colour. Cationic lignin did not improve the foam stability much compared to kraft lignin, but provided a similarly dark brown colour. Chlorophyll provided the foams with a light green colour that did not resemble the natural colour in many plants.

This work was a first proof-of-concept and the aim was to screen a large amount of parameters, hence one drawback is the lack of statistical consideration. However, it can be noted that later performed repetitive investigations of the most promising systems confirm the main conclusions drawn here. In this work the foams were produced in small, lab scale with a homogenizer. More research is needed to optimize the foam production at large scale. Possible modifications to make the foams resistant to weathering and outdoor conditions should be further investigated.

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